ELECTROLYTIC OXIDATION OF ANILINE OIL.

By Toyokichi YASUI.

Received April 2nd, 1935. Published August 28th, 1935.

In 1856, Perkin discovered the first coal-tar dye, mauve; various oxidizing agents were used by different investigators for producing the red dyes from the crude aniline. It is well known that by the strong oxidizing agents mauve is produced, and by the weak oxidizing agents fuchsine is produced.

The author has intended to ascertain what kind of the red dye is produced by the electrolytic oxidation of the crude aniline.

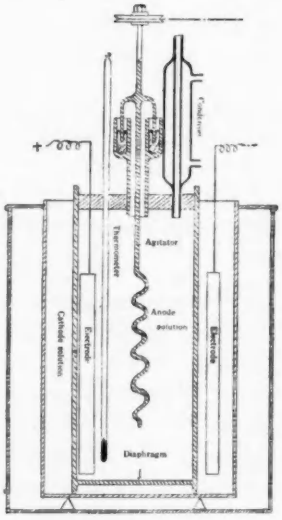


Fig. 1.

The experimental apparatus is shown in Fig. 1. Experimental conditions were as follows: Reagents taken, aniline 15.5 g., *o*-toluidine 17.7 g., and *p*-toluidine 17.7 g. Anode solution, aqueous solution of mineral acid salts of the reagents. Cathode solution, aqueous solution of mineral acid. Electrode, carbon plate. Diaphragm, cylindrical porous cell. Current density, 2 amp./100 sq. cm. Temperature, 80°–90°C. Voltage, 5–6 volts.

I. Quantity of Electricity and Depth of Colour. Under the above conditions, the electrolytic oxidation was applied to aniline oil with a constant agitation of the anode solution. The anode solution became red in short time and by continued treatment it passed into yellow, and finally lost the dying property.

This red dye is difficultly soluble in cold water, fairly soluble in hot water; with alkali it yields a brown precipitate. Its solubility in acid is proportional to the acid concentration, and it becomes colourless by reduction and is gradually recoloured in the air. From these properties it does not belong to triphenylmethane dyes and we may suppose it belongs to the azine group.

At the beginning of the electrolysis, the yield of the dye is proportional to the quantity of electricity; by a further passage of the electrical current the concentration is rather decreased and it is decomposed into foreign substances.

II. Investigation of Absorption Spectrum. It is well known that mauve, safranine, and fuchsine are produced by the oxidation of aniline oil. By comparing the absorption spectra of these dyes with that of the dye which is produced by the electrolytic oxidation, it may be ascertained that the new dye belongs to the series of these dyes, and it is recognized as an intermediate product from the spectra taken at intervals during the oxidation. The absorption curves are shown in Fig. 2. From these curves the dye produced by the electrolytic oxidation is none of mauve, safranine, and fuchsine, but it is situated between mauve and safranine or fuchsine.

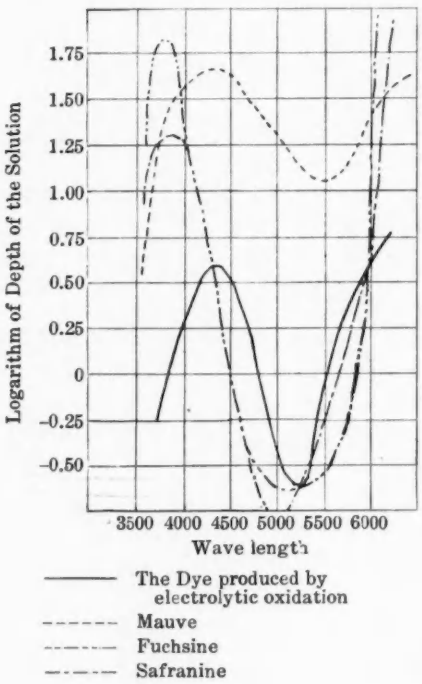


Fig. 2.

At the beginning of the oxidation the absorption takes place at the indigo part and it moves to the purple part, but no definite intermediate product can be recognized by the curves.

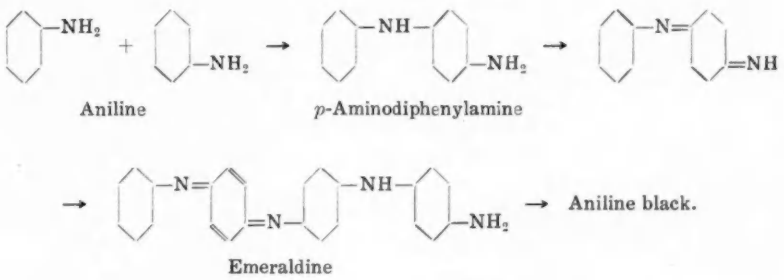
III. The Intermediate Product. From the absorption curves no definite intermediate product can be recognized even though the curves move with progressing oxidation.

By the electrolytic oxidation in the cold, say below 10°C., a blue precipitate is produced, which is scarcely soluble in cold water, fairly soluble in hot water, and easily soluble in alcohol.

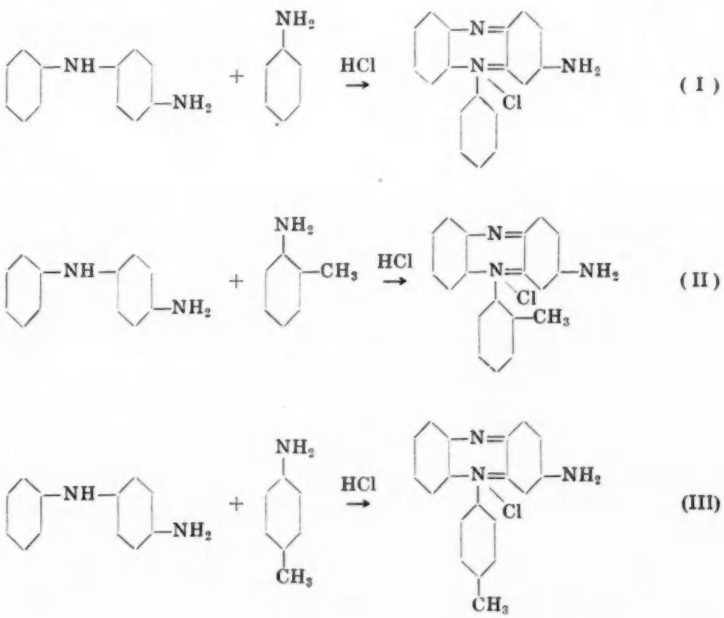
To ascertain the composition of the blue precipitate aniline was first subjected to the electrolytic oxidation at 5–7°C.; the blue precipitate which was soon formed was drawn out from the solution and purified by washing. This blue substance is the same as quinonanil (emeraldine) in all behaviours, which is produced by the ordinary oxidation of aniline.

Examination of the properties of the ether soluble substance leaves no doubt that it is *p*-aminodiphenylamine, but the quantity was too small for crystallization.

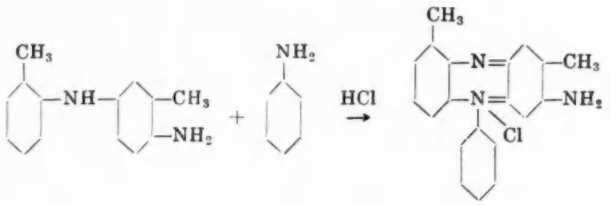
The following equations show the process of the electrolytic oxidation of aniline:



p-Aminodiphenylamine reacts with anilines and produces the red dye, apo-safranine:



The *p*-aminodiphenylamine produced from *o*-toluidine reacts with aniline, *o*-toluidine, and *p*-toluidine in the following manner:



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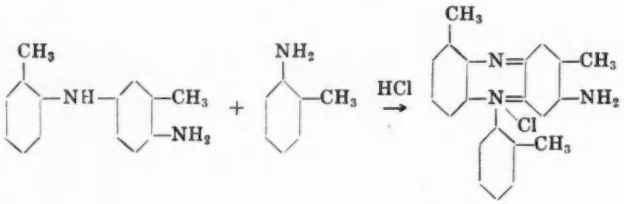
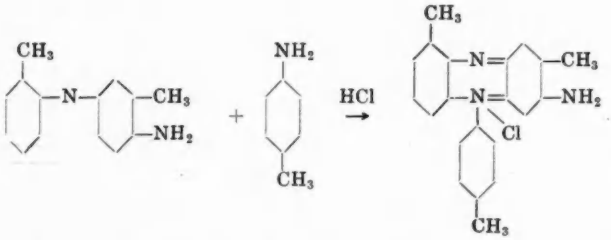


(V)

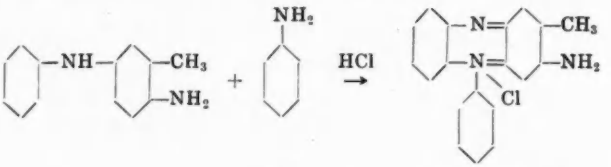


(VI)

From *p*-toluidine no blue precipitate can be produced. In this case, the basic dyes of reddish-violet are Barsilowsky's and Perkin's bases.

$(C_7H_7N)_3$ (VII) $(C_7H_7N)_3$ (VIII)

The *p*-aminodiphenylamines from aniline and *o*-toluidine react with aniline, *o*-toluidine, and *p*-toluidine in the following manner:



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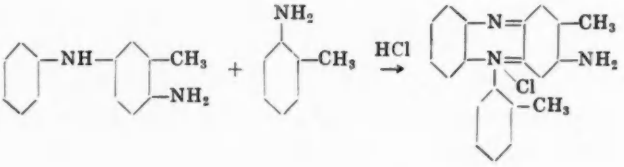
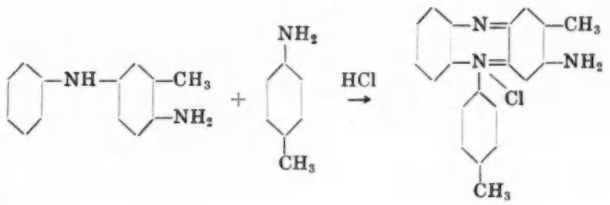


(X)



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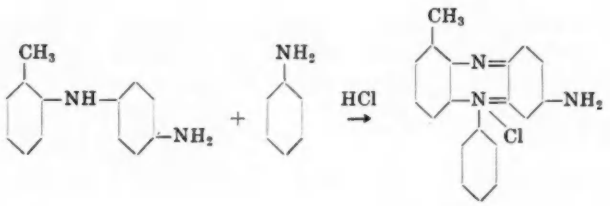

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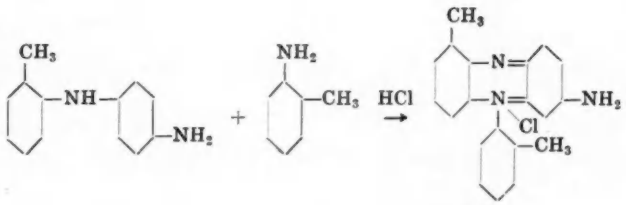
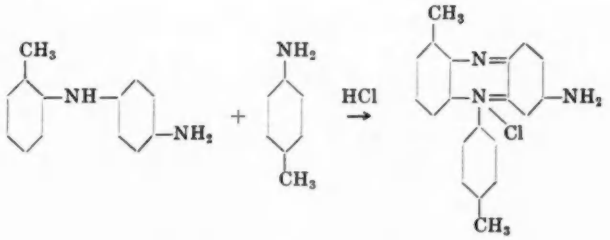
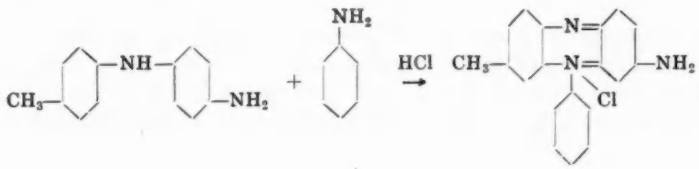


(XIII)



(XIV)

The *p*-aminodiphenylamine from aniline and *p*-toluidine reacts with aniline, *o*-toluidine, and *p*-toluidine as follows:



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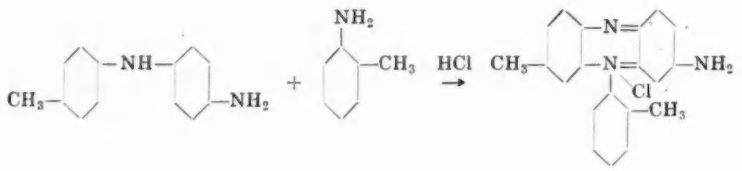

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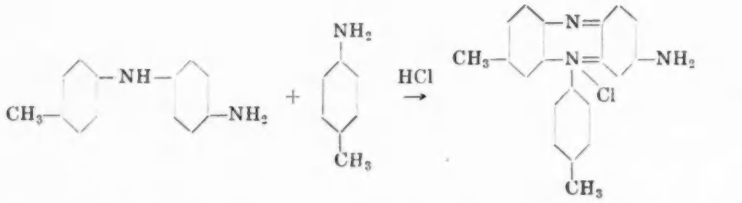
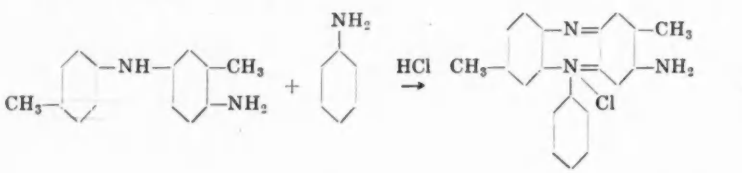


(XVII)

The *p*-aminodiphenylamine from *o*-toluidine and *p*-toluidine reacts with aniline, *o*-toluidine, and *p*-toluidine as follows:



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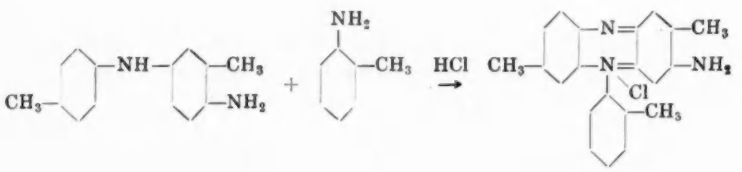

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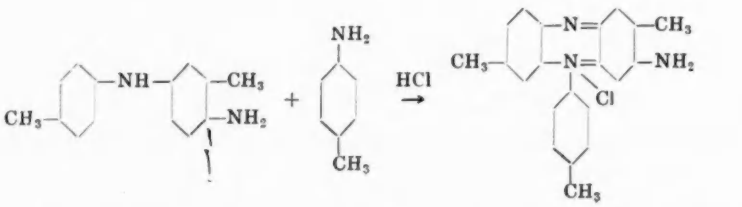

(XX)

As described above, there are produced 20 kinds of the red dyes by the electrolytic oxidation of aniline oil. Among them (II), (III), (IX), (XII), and (XV) form one group of isomers, (IV), (X), (XI), (XIII), (XIV), (XVI), (XVII), and (XVIII) another group and (V), (VI), (VII), (XIX), and (XX) a third group.

Summary.

(1) By the electrolytic oxidation of aniline oil in acid solution neither safranine nor fuchsine is produced.

(2) *p*-Aminodiphenylamine is first produced, it passes into emeraldine and finally into aniline black.

(3) *p*-Aminodiphenylamine reacts with aniline and homologues producing aposafranine.

The author wishes to express his sincere thanks to Dr. M. Matsui, President of the Imperial University of Kyoto, for his kind encouragement and valuable advices given in the course of these studies.

(October 30th, 1933)

Chemical Laboratory,
Fukui College of Technology.

ELECTROLYTIC REDUCTION OF SUCCINIMIDE.

By **Buhei SAKURAI.**

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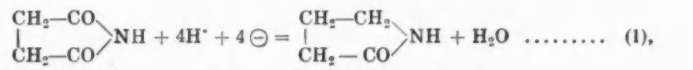
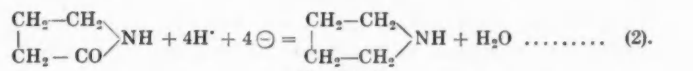
When succinimide is subjected to reduction, it is supposed, in the first stage one of its carbonyl groups undergoes reduction giving rise to the formation of pyrrolidone, and then, by further strong reduction, the other carbonyl group is reduced, pyrrolidine being produced as the complete reduction product:





Many researches have already been reported on the reduction of succinimide, both chemical and electrolytical, with a view to obtain pyrrolidine.

For instance, A. Ladenberg[1] reduced succinimide chemically with metallic sodium in a solution of pure ethyl alcohol, and obtained a small quantity of pyrrolidine. J. Schnick[2] used amyl alcohol in place of ethyl alcohol with a little increase in the yield of pyrrolidine.

J. Tafel[3] attempted an electrolytic reduction with lead cathode of strong reducing ability in solution of 50% sulphuric acid and with very high current density, and obtained pyrrolidone, the product formed by the reduction of only one of the two carbonyl groups. E. Späth[4] also tried a similar electrolysis with derivatives of succinimide and obtained a fair yield of reduction products corresponding to pyrrolidine. Thus the reduction of succinimide itself has been considered more difficult than that of its derivatives.

As the present writer previously recognized the stronger reducing power in zinc amalgam cathode than in lead cathode, he applied it to the projected reduction of succinimide and succeeded in obtaining a pretty good result with a greater yield than in any foregoing experiments.

The cathode for the reduction of such a difficultly reducible substance must be made with an extremely pure material in order to acquire a high reducing power, and, therefore, metals with impurities and consequently with lower overvoltage must not be used. The cathode of zinc amalgam used was made as pure as possible in the following manner. An unglazed cylindrical cell 5 cm. in diametre and 15 cm. in height, which had been prepared with special care as to material, was treated with hot dilute hydrochloric acid for several days until it had no colour. Thus all impurities were dissolved away. Then 250 g. of redistilled pure mercury from E. Merck was introduced into the cylinder and a saturated aqueous solution of pure zinc sulphate also from E. Merck was poured on it. This cell was put in a glass vessel containing pure dilute sulphuric acid and a lead electrode. Zinc was produced by electrolysis on the surface of the mercury as cathode and the lead as anode. When the electrolysis went far enough and the mercury solidified into a sponge-like substance, it was stopped. Zinc amalgam thus prepared was used in the experiments.

The conditions of electrolysis were as follows: Cathode, zinc amalgam, 15 sq. cm.; cathodic solution, 100 c.c. of 50% H_2SO_4 from E. Merck; anode, cylindrical lead; anodic solution, pure 50% H_2SO_4; current density, 100 amperes for 100 sq. cm.; temperature, 38°–40°; time of electrolysis, 6 hours.

Succinimide (10 g.) was introduced into the cathodic solution and the solution was electrolysed with vigorous agitation. The cathodic solution was

(1) *Ber.*, **20** (1887), 2215.
(2) *Ber.*, **32** (1899), 952.
(3) *Ber.*, **33** (1900), 2224; *Z. physik. Chem.*, **35** (1905), 433.
(4) *Mona sh.*, **50** (1928), 349.

cooled during electrolysis by passing cold water through a lead tube inserted in the porcelain cylinder, and the vessel was placed in circulating cold water. The imide dissolved after a little while into a transparent solution. For about half an hour from the beginning the evolution of hydrogen gas was very slight, indicating a smooth reduction. Then the evolution of hydrogen gas increased gradually. When the electrolysis was over, the cathodic solution was taken out and made weakly alkaline with caustic soda solution under cooling in cold water. The characteristic odour of pyrrolidine, the complete reduction product, was set free, and red litmus paper brought near turned blue at once, indicating the presence of a volatile base.

Then the solution was subjected to steam distillation and pyrrolidine distilled off easily with steam. The distillation was continued until red litmus paper changed its colour no more. As pyrrolidine is easily soluble in water, the distillate was a dilute aqueous solution of it. After neutralization of this solution with hydrochloric acid and evaporation on a water bath there remained 1.5 g. of the hydrochloride of pyrrolidine, which corresponded to 14% of the theoretical yield. The gold salt of pyrrolidine which was precipitated on addition of gold chloride melted at 205°. Found : Au, 47.85. Calc. for $C_4H_9N \cdot HCl \cdot AuCl_3$; Au, 47.95%.

The residual solution in the distilling flask was precisely neutralized with sulphuric acid, and after sodium sulphate, which crystallized on cooling the solution, was removed, pyrrolidone, the partial reduction product, remained as an oily substance. It was extracted with ether and 5 g. of crude pyrrolidone was obtained after the removal of the ether. When it was distilled, pure pyrrolidone distilled over at 250°. In a cold place it became crystals melting at 25°.

When succinimide was electrolysed for 12 hours, other conditions being the same as before, the yield of pyrrolidine increased to 28%. If the electrolysis takes place at above 60° and the concentration of sulphuric acid is 50%, succinimide decomposes into succinic acid and ammonia.[5] If sulphuric acid of 65% or over be used, the decomposition happens more easily. If the sulphuric acid is 30% or under, the decomposition does not happen even at 80°, while no reduction takes place.

The writer expresses his sincere thanks to Dr. Motooki Matsui, President of the Imperial University of Kyoto, at whose suggestion this work has been carried out.

(February 17th, 1934)

Chemical Institute, Osaka Women's College,
Sumiyoshi, Osaka.

(5) Pannain, *Gazz. chim. ital.*, **35**, II, 94.

ON THE INDUCED REACTION.

By Riki HORIUCHI.

Received April 2nd, 1935. Published August 28th, 1935.

Since an observation regarding the induced reaction appeared in Mohr's text-book (1855), many chemists have treated it, but its theory still remains unknown. Further, the induced reactions so far described appear to be limited to oxidation reactions, and they are called induced oxidation in other words.

The writer, in the course of a study of isomerization of eugenol and safrol, has discovered an induced reaction, which differs in its nature from any known before, and he has shown it to be a kind of catalytic action.(1)

For the isomerization of safrol into isosafrol, caustic potash is usually used as catalyst, heat being applied at the same time. But, eugenol is difficulty isomerized by the same treatment and gives sometimes a resinous matter, but the reaction generally does not take place. On the other hand, if eugenol is mixed with safrol and treated with caustic potash as in the case of safrol transformation, eugenol is smoothly isomerized into isoeugenol, safrol being transformed into isosafrol at the same time. Further, experiments have shown that when eugenol and safrol are mixed together, not only eugenol but also safrol are completely isomerized at such a low temperature as would not cause the formation of isosafrol if safrol exists alone. The isomerization of eugenol may be considered to become easy owing to any one of the three following causes: (1) either safrol or isosafrol is a suitable solvent for eugenol; (2) either safrol or isosafrol catalytically accelerates the isomerization of eugenol; (3) the isomerization of safrol induces the isomerization of eugenol.

In order to ascertain which one of these was the real cause, the writer used various solvents as substitutes for safrol, but no positive result was obtained. Even if isosafrol was used as the solvent, the result was negative. It could not be considered that eugenol isomerization was due to the catalytic action of safrol, because safrol becomes isosafrol promptly. Therefore, for the explanation of eugenol isomerization it must be considered that the isomerization of eugenol is accelerated by the isomerization of safrol in the presence of caustic potash; in other words this phenomenon is an induced reaction, where the primary reaction with safrol as inducer and caustic potash as actor accelerates the reaction of caustic potash and eugenol as

(1) *J. Chem. Soc. Japan*, **45** (1924), 209.

acceptor. This view has naturally extended the induced reaction to isomerization beyond oxidation.

A very interesting fact is that, irrespective of the quantity of safrol, and thus in spite of much smaller quantity of safrol compared with that of eugenol, the latter isomerizes vigorously. Not a few authors have explained the mechanism of the induced reaction as consecutive reaction; but, taking into account such views as that of Mellor[2] represented by the formula

$$\text{Induction factor} = \frac{\text{Amount of acceptor transformed}}{\text{Amount of inducer transformed}},$$

it is possible to increase the induction factor to a very large quantity, and the experimental results of the writer have evidently verified that this induced reaction is a catalysis.

The writer, desiring further to extend the above theory to general reactions, has obtained another example.[3] Diphenyl oxide is formed in the reaction expressed by the following equation, copper powder being used as a catalyst:

$$C_6H_5OK + C_6H_5Br = C_6H_5OC_6H_5 + KBr.$$

In case sodium phenolate is used instead of potassium phenolate, the reaction velocity is extremely reduced, but if potassium phenolate and sodium phenolate are mixed together, the reaction proceeds more rapidly than when they are used separately, just in the same manner as the mixture of safrol and eugenol is isomerized by caustic potash.

For such an induced reaction, the writer proposes the name "mutually induced reaction". He considers that, in this case, the relation of the primary reaction to the secondary will be just the same as the relation of the secondary to the primary, each accelerating and promoting the other.

Besides, the writer has given elsewhere many examples of induced reactions and verified that they are all mutually induced reactions.[4] A list of examples including the above-mentioned is given in Table 1.

Table 1.

Primary reaction	Secondary reaction	Actor	Inducer	Acceptor
Safrol+KOH	Eugenol+KOH	KOH	Safrol	Eugenol
Eugenol+KOH	Safrol+KOH	KOH	Eugenol	Safrol
KOH+Eugenol	NaOH+Eugenol	Eugenol	KOH	NaOH
KOH+Safrol	NaOH+Safrol	Safrol	KOH	NaOH
$C_6H_5OK+C_6H_5Br$	$C_6H_5ONa+C_6H_5Br$	C_6H_5Br	C_6H_5OK	C_6H_5ONa

(2) "Chemical Statics and Dynamics", (1904), 333.

(3) *J. Chem. Soc. Japan*, **47** (1926), 368.

(4) *J. Chem. Soc. Japan*, **47** (1926), 357; *ibid.*, **48** (1927), 171.

As given in the table, in these induced reactions, the constitutions and chemical properties of the inducer and the acceptor resemble each other. In view of these facts, the writer has made further experiments by mixing substances of similar constitutions and has obtained an unexpected result of an induced reaction.[5] By the action of dilute sulphuric acid citronellal produces a large quantity of isopulegol, while citral, a minute quantity of dehydroisopulegol. The writer has, therefore, treated the mixture of these two substances in the same way with the expectation that, by induction, these two alcohols might be formed in larger quantities; but, on the contrary the reaction proceeded to an entirely different direction, and each formed a pinacone. These pinacones have not yet been recorded and the writer named them dicitronellal pinacone, $(C_{10}H_{17})_2(OH)_2$, and dicitral pinacone, $(C_{10}H_{15})_2(OH)_2$, respectively. They are formed in large quantities in the above reaction, which affords a good example of the formation of two similar substances from two other similar substances.

To sum up, the induced reaction is explained by the writer in the following manner. When two homologous substances or substances of similar structures are mixed, they catalyze each other, and similar reactions always take place. If one of the two substances reacts with a third substance, they act as inducer and acceptor to each other, and this action accelerates the reaction to a further extent and thus causes induction. In other words, in these induced reactions, the fundamental condition is that the inducer and the acceptor must have a resemblance in chemical structure and properties.

Having found such a fundamental feature of the induced reaction, the writer has made an observation in some usual catalytic actions. As shown in Table 1 the isomerization of eugenol is an induced reaction, in which caustic potash and caustic soda mutually act as inducer and acceptor, but this induced reaction may be described as a catalytic action with caustic soda as catalyst and caustic potash as promotor. Consequently, an induced reaction of this kind is nothing but a catalysis with a promotor. With this view, the writer has investigated the reactions formerly considered mere promotor reactions and found an interesting fact. For instance, it is known that in the ammonia synthesis catalyzed by iron, if molybdenum, tungsten, uranium, etc. are used as promotor, the catalystic activity of iron increases, thus accelerating the velocity of the formation of ammonia. In the case of formation of hydrogen from water gas, $CO+H_2O = CO_2+H_2$, the velocity of formation is said to be greater if the oxides of nickel, chromium, etc. are used as promotor with iron catalyst than if iron alone is used. Further, in the case of producing aniline black from aniline, *p*-diamine or *p*-aminophenol is

(5) *Ibid.*, **47** (1926), 417.

used with vanadium salt as catalyst. In the two former instances, the resemblance in the properties between the catalyst and the promotor is quite clear from the periodic system. In the last instance, although the promotor does not resemble the catalyst, it possesses properties similar to those of aniline, the subject of the reaction.

If the above examples are considered in the light of the writer's opinion that two similar substances mutually act as inducer and acceptor on each other and can cause an induced reaction, it is conceivable that these promotor reactions can also be described as induced reactions.

The writer wishes to extend the observation to catalytic actions in general. The above-described induced formation of diphenyl oxide is conceivable as a reaction of sodium phenolate and bromobenzene catalyzed by potassium phenolate. Or again, the isomerization of eugenol, if this be described as a reaction of eugenol and sodium hydroxide, may be said to be a catalysis by potassium hydroxide. Thus, these induced reactions may be considered as ordinary catalytic actions.

The formation of dicitronellal pinacone appears to be slightly different from the above. As a rule, citronellal yields isopulegol in the reaction with sulphuric acid, but, when it is mixed with citral, the formation of isopulegol is retarded exceedingly, and on the other hand, the reaction is directed toward the formation of dicitronellal pinacone which induces the formation of dicitral pinacone. If this induced reaction is considered a catalytic action by citral, then citral acts poisonously on the formation of isopulegol, that is to say, as a negative catalyst. Consequently, the induced reaction given above involves not only positive but also negative catalysis.

These explanations will show that many examples of catalytic actions, whether positive or negative, and of promotor actions can be described as induced reactions in the sense defined by the writer, that is, reactions taking place when two similar substances are mixed together.

How can the mechanism of this new and particular induced reaction be explained? The radiation theory of reactions proposed by Perrin or C. W. Lewis was once valued as an interesting hypothesis, but the experiments do not support it. If the radiation theory is applied to the present case, it appears that the explanation may be given easily on the basis that the particular radiation emitted by the primary reaction has induced the secondary reaction. However, in this case also, there is no experimental fact to support the hypothesis. Furthermore, the fact that the induction factor can be enlarged to infinity brings about the difficulty that the induced reaction must be considered as a photo-chemical chain reaction. These facts lead the writer to the consideration that this catalytic action may be solved by the

collision theory with the special steric factor taken into account. The writer will further make quantitative experiments and desires to study carefully the mechanism.

At any rate, in view of chemical synthesis, this induction may be utilized to accelerate the reaction velocity; or in the absence of any known standard for the choice of a catalyst, a consideration of the induction may now give some suggestions for this purpose.

Summary.

(1) The induced reaction, which was formerly limited to oxidation reaction, has been extended to reactions in general, and many examples have been given.

(2) All these induced reactions have been proved to be catalytic actions.

(3) Evidences have been given to show that among catalytic actions, positive or negative, and promotor actions, there are many instances which can be described as induced reactions.

(4) It has been shown that these induced reactions must always have two similar substances as inducer and acceptor.

The above thesis is based upon many experiments made since 1924 under the guidance of Dr. Matui, President of the Imperial University of Kyoto. The writer has also been given many valuable advices by Prof. Horiba. He wishes to express his hearty thanks to them.

(April 20th, 1934)

Takasago Perfumery Company, Ltd.,
Kamata, Tokyo.

ON THE STRUCTURE OF NAPHTHALENE NUCLEUS.

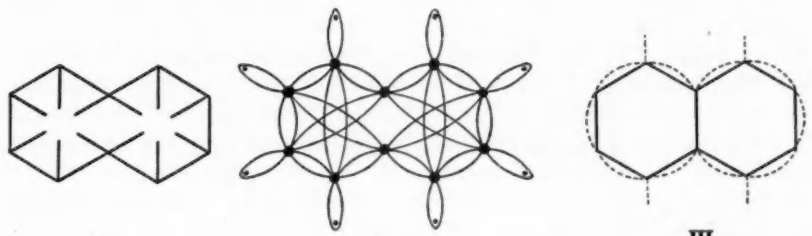
By Nobuo NAKATA.

Received April 2nd, 1935. Published August 28th, 1935.

Although many attempts were made to assign a structural formula to naphthalene, there is much uncertainty in this problem. As an introduction to my own experiments,[1] on which I will report shortly, I have tried to obtain a clear notion on the status of the problem.

(1) *Ber.*, **64** (1931), 2059.

The structural arrangement of the carbon atoms is proved by many syntheses, but the distribution of the five double bonds is very doubtful. This question is identical with the problem of the aromatic nature of the naphthalene system. Bamberger,[2] signifying the analogy between benzene and naphthalene, proposed formula (I) with centric valencies, which in terms of the modern electronic theory of valency is the renewed formula by L. Pauling (II).[3] But these formulæ give no account of the well-known fact that naphthalene does not possess the same degree of aromatic nature as benzene. By the usual substitution reagents naphthalene is very easily attacked, and our model must explain such irregularities.



I II III

The application of Thiele's theory of partial valencies to naphthalene formula (III) can doubtlessly account for the unusual reactivity of the α-positions. But, since the properties of anthracene are not explained by Thiele's theory without the hypothesis that the meso-carbon-atoms are tervalent, it seems also uncertain to work with Thiele's theory in the naphthalene series. Furthermore, formula (III), cannot account for the very surprising fact that the 3-position is not an ortho-position to the 2-position. For instance, 2,3-dihydroxy-naphthalene cannot be converted into a quinone, while the 1,2-compound can and, on coupling with diazonium-compounds, β-naphthol reacts at an α-position, but by no means at any of the β-positions. The very profound spectrochemical data, collected on naphthalene compounds by K. v. Auwers and his collaborators,[4] lead to the conclusion that the physical and chemical properties of this hydrocarbon are explained by Erlenmeyer's formula (IV) with nuclei, one aromatic and the other partly hydroaromatic. The investigation by Bhatnagar and Singh[5] on the parachor value of

(2) *Ann.*, **257** (1890), 1.

(3) *J. Am. Chem. Soc.*, **48** (1926), 1140.

(4) Auwers and Frühling, *Ann.*, **422** (1920), 192; Auwers and Krollpfeiffer, *ibid.*, **430** (1923), 230.

(5) *J. Indian Chem. Soc.*, **6** (1929), 263.

IV V VI a VI b

naphthalene seems also to demonstrate that it is not a homogeneously aromatic system, but really consists of two different rings. However, formula IV is interpreted by Auwers as not representing a rigid system, but as being in a mobile equilibrium with formula V, in which the ring on the right is aromatic, whereas in the system IV the left ring has a benzenoid character. This interpretation corresponds to the oscillation hypothesis for explaining the fact that only one *o*-dichloro-benzene exists (VI a, VI b). The generalization proposed by Auwers is by no means a progress in the naphthalene chemistry. The previously mentioned fact that the 1,2-, but not the 2,3- positions are really ortho-positions cannot be understood if we assume the equilibrium between IV and V. Only when we make the special assumption that those exclusively combined by a double linkage are ortho-positions and when we, in the second place, attribute the rigid formula IV to naphthalene, we can explain the anomaly in question, an anomaly, indeed, which induced Obermiller[6] to deny the existence of a real bond between the carbon atoms 2 and 3 and between carbon atoms 6 and 7. The difficulty is deepened by the observation of H. de Làszlò[7] that the carbon atoms 2 and 6 are not wholly identical with the carbon atoms 3 and 7 respectively.

There is another question concerning the stereochemical behaviour of naphthalene. Are all the carbon atoms of each ring placed on one plane or are the two rings in our system on the same plane? The observation of Bragg[8] that naphthalene has only one center of symmetry in its crystal is interpreted by E. Bergmann and Mark[9] on the basis of the fact that benzene in its crystalline state is represented by a puckered ring, in which carbon atoms lie alternatingly in two planes. The same assumption for the naphthalene nucleus gives really a centrosymmetrical model. But we must add that the carbon atoms can vibrate between the two possible extreme positions.[10] This statement is confirmed by Mack[11] on measurements of

(6) *J. prak. Chem.*, (2), **126** (1930), 257.
(7) *J. Am. Chem. Soc.*, **50** (1928), 892.
(8) W. H. and W. L. Bragg, " X-Rays and Crystal Structure ", p. 230.
(9) *Ber.*, **62** (1929), 750.
(10) Cf. Richard Kuhn, *Ann.*, **475** (1929), 13.
(11) *J. Am. Chem. Soc.*, **47** (1925), 2468.

the area of the gaseous naphthalene molecule. The centrosymmetry of naphthalene excludes also the possibility that the two rings do not lie in the same plane, an assumption made by Kaufler[12] many years ago. But we must remember the possibility that not all naphthalene derivatives have the same structure, a supposition already expressed by Willstätter.[13]

It seems desirable to make new experiments for elucidating the state of affairs. The method applied by me to the problems in question is the measurement of dipole moments, which has led to very interesting results in the field of organic chemistry.[14]

The moments measured are given in Table 1. The experimental details will be published elsewhere. The comparison between the α-substituted naphthalenes and the corresponding benzene derivatives (nitrobenzene 3.96, fluorobenzene 1.45, chlorobenzene 1.56, bromobenzene 1.49[15]) leads to the very surprising conclusion that only the α-positions of the naphthalene nucleus have an aromatic character. The moments of the isomeric β-compounds are higher, and since the aliphatic halogen atoms have higher moments than the aromatic, we must conclude that the β-positions of naphthalene have aliphatic character. The carbon atoms 2 and 3 are ethanoid, and here is the explanation for the mentioned anomaly of the 2,3-compounds, an explanation which demonstrates, I believe, the correctness of formula IV.

Table 1.

Substance	Dipole moment in 10^{18} electrostatic units	Substance	Dipole moment in 10^{18} electrostatic units
α-Nitronaphthalene	3.88	1,4-Dichloronaphthalene	0
α-Fluoronaphthalene	1.42	1,5-Difluoronaphthalene	~0
α-Chloronaphthalene	1.50	1-Bromo-5-nitronaphthalene	2.49
α-Bromonaphthalene	1.48	2,8-Dichloronaphthalene	2.58
β-Fluoronaphthalene	1.49	2,6-Dichloronaphthalene	0.60
β-Chloronaphthalene	1.57	1-Bromo-2-fluoronaphthalene	2.34
β-Bromonaphthalene	1.69	1-Bromo-2-iodonaphthalene	1.80

The centrosymmetry of naphthalene is demonstrated by the moments of 1,4-dichloronaphthalene, 1,5-difluoronaphthalene and 1-bromo-5-nitronaphthalene. In a centrosymmetrical model the partial moments of the

(12) *Ann.*, **351** (1907), 151; *Ber.*, **40** (1907), 3250.

(13) *Ber.*, **56** (1923), 1407.

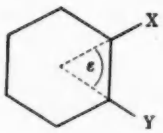
(14) Cf. E. Bergmann and L. Engel, *Z. physik. Chem.*, (B), **8** (1930), 111.

(15) Bergmann, Engel, and Sándor, *Z. physik. Chem.*, (B), **10** (1930), 106, 397.

substituents in the α-positions must be additive, and in the former two compounds they compensate one another; the moments of the latter substance must be equal to the difference of the nitro-group and bromine, namely $3.98-1.49=2.49$, what comes true indeed. The moment of 2,8-dichloronaphthalene has also the expected value. It results from the moments of chlorine in α- and β-positions, respectively, by vectorial addition in an angle of 60°, postulated by the model.

Therefore, it is very surprising that 2,6-dichloronaphthalene has not a zero moment.[16] If other compounds of the same type, which are under investigation, have also a definite moment, we must conclude that in these compounds the naphthalene system is not "uniplanar", but folded.

The investigation of naphthalene derivatives must be pursued. I believe that the most interesting question is the relation between neighbouring atoms and their mutual influence. Therefore, I have measured also the moments of 1-bromo-2-fluoro- and 1-bromo-2-iodo-naphthalene. Bergmann, Engel, and Sándor have exactly proved that the neighbouring atoms in *o*-dihalogenobenzenes repel one another on account of their "Raumbeanspruchung", which increases in the order $F<Cl<Br<I$. The angle between the ortho-valencies, which is normally 60°, increases, and the dipole moment of the compound therefore decreases. The dipole moment of the compound is calculated by the equation

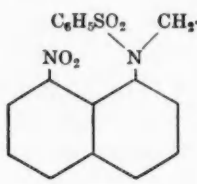


$$\mu^2=\xi^2+\eta^2-2\xi\eta\cos(180-\varepsilon);$$

hence

$$\varepsilon=\arccos\frac{\mu^2-\xi^2-\eta^2}{2\xi\eta}.$$

It is very interesting that on comparison of the two di-halogenated naphthalene derivatives mentioned, with *o*-bromo-fluoro-benzene and *o*-bromo-iodobenzene the angles between the ortho-valencies are almost same (80 and 97° in the benzene series, 76 and 105° in the naphthalene compounds).



It is a well-known fact that also the 1,8-positions in naphthalene are in a certain measure ortho-positions; the very great influence between them is best demonstrated by the resolution of the compound:[17] Höjendahl[18] has measured the moment of 1,8-dinitronaphthalene. If we assume the found value (7.1) to be correct, we must

(16) *Loc. cit.*
(17) Mills and Elliot, *J. Chem. Soc.*, **1928**, 1291.
(18) *Physik. Z.*, **30** (1929), 391.

conclude that the valencies are not parallel to one another, but make—on account of the "Raumbeanspruchung" of the nitro-groups—an angle of ca. 50°. In this question further investigations will bring many interesting informations.

(June 15th, 1934)

SOME NEW DERIVATIVES OF PROTOCATECHUIC ACID FORMED FROM SAFROL AND TWO EXAMPLES OF THE REARRANGEMENT OF THE ACYL GROUP.

By **Kashichi ONO** and **Minoru IMOTO.**

Received May 10th, 1935. Published August 28th, 1935.

Many investigations have already been made on treating safrol (I) with methanol and caustic alkali for splitting off the methylene-dioxy group and thus obtaining methoxy-isoeugenol (II) and methoxy-isochavibetol (III).[1] On protocatechuic acid derivatives (X) formed from them, some detailed work has been published by Hirao[2] of our laboratory of the Nippon Koryo Yakuhin Kaisha, Ltd., Kobe. The commercial production of vanillin from safrol is practiced by our company by this method on a large scale. The present paper deals with the synthesis of new acids by acetylation, benzoylation, and oxidation of a mixture of phenolic compounds of II and III.

The mixed phenolic compounds II and III are obtained from safrol by treatment with methanol and caustic alkali under pressure. If acetic anhydride alone is used for acetylation, diacetate is formed, while, if anhydrous sodium acetate is also added to a large excess of acetic anhydride, the monoacetates alone are formed. When benzene was used as solvent, there was no reaction observed to take place, while, by taking xylene as the solvent, monoacetate was the principal product. By addition of a drop of concentrated sulphuric acid, diacetate alone is produced.

The authors have succeeded easily in crystallizing out methoxy-isochavibetol benzoate (XIV) by employing the method used by Hirao, namely,

(1) G. Ciamician and P. Silber, *Ber.*, **23** (1890), 1162; S. Nagai, *J. Soc. Chem. Ind., Japan*, **27** (1924), 631; N. Hirao, *J. Chem. Soc. Japan*, **51** (1930), 441; T. Hiraizumi, *J. Soc. Chem. Ind., Japan*, **34** (1931), 584; T. Kuwata, *ibid.*, **34** (1931), 590.

(2) *J. Chem. Soc. Japan*, **51** (1930), 713; *ibid.*, **54** (1933), 194, 992; etc.

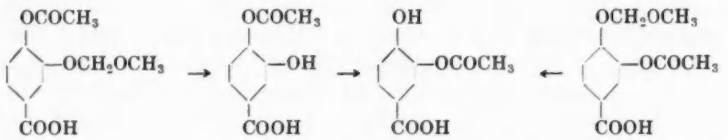
by dissolving the decomposition products of safrol with potassium hydroxide, shaking the solution with benzoyl chloride, treating the soft lump of mixed benzoates with alcohol, and crystallizing out methoxy-isoeugenol benzoate (XIII). The mother liquor contains the compound XIV, which crystallizes out on allowing the mother liquor to stand for about three days. Its m.p. is 55°.

The filtrate from XIII and XIV deposits, when concentrated on the water bath and allowed to stand, propenyl-pyrocatechin benzoate (XV).

When the diacetate of propenyl-pyrocatechin was oxidized with neutral or alkaline potassium permanganate, a resinous product alone was obtained. Both monoacetates (V and VI) could also be oxidized only in acid solution. The monobenzoates XIII and XIV could, however, be oxidized in neutral medium showing that benzoyloxy group is not so easily saponified as acetoxyl group. In this manner, besides the previously known diacetoxy-benzoic acid (VII) the following four new acids were obtained:

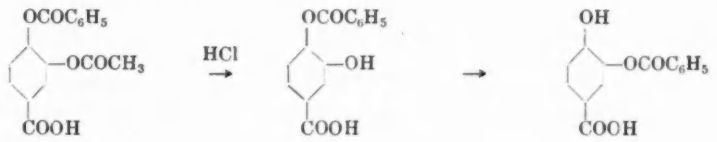
VIII 4-Acetoxy-3-(methoxy-methoxy)-benzoic acid, m.p. 112–113°;
IX 3-Acetoxy-4-(methoxy-methoxy)-benzoic acid, m.p. 150–152°;
XVI 4-Benzoyloxy-3-(methoxy-methoxy)-benzoic acid, m.p. 127°;
XVII 3-Benzoyloxy-4-(methoxy-methoxy)-benzoic acid, m.p. 117–118°.

Diacetoxy-benzoic acid was saponified by concentrated hydrochloric acid into protocatechuic acid (X) and the latter was changed by benzoylation by the Schotten-Baumann method into a new compound, dibenzoyloxy-benzoic acid benzoylester (XII). The compounds VIII and IX were changed by splitting off the methoxy-methoxy group by treating with acids into a compound melting at 198° corresponding to 3-acetyl-protocatechuic acid (XI) synthesized by Ciamician and Silber,[1] and E. Fischer, M. Bergmann, and W. Lipschilz,[3] and melting at 197–199°. Evidently a rearrangement of the acyl group has taken place:

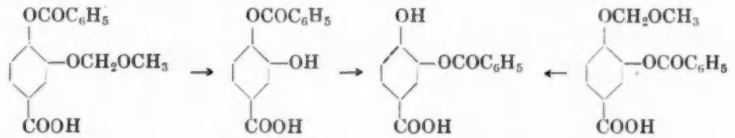


Such a rearrangement of the acyl group has been observed already by various workers, and the present authors have also obtained, by a similar splitting of the methoxy-methoxy group from XVI and XVII, the same compound with melting points 224° and 225°, corresponding to 3-benzoyl-protocatechuic acid (XVIII) obtained by E. Fischer by the following rearrangement:

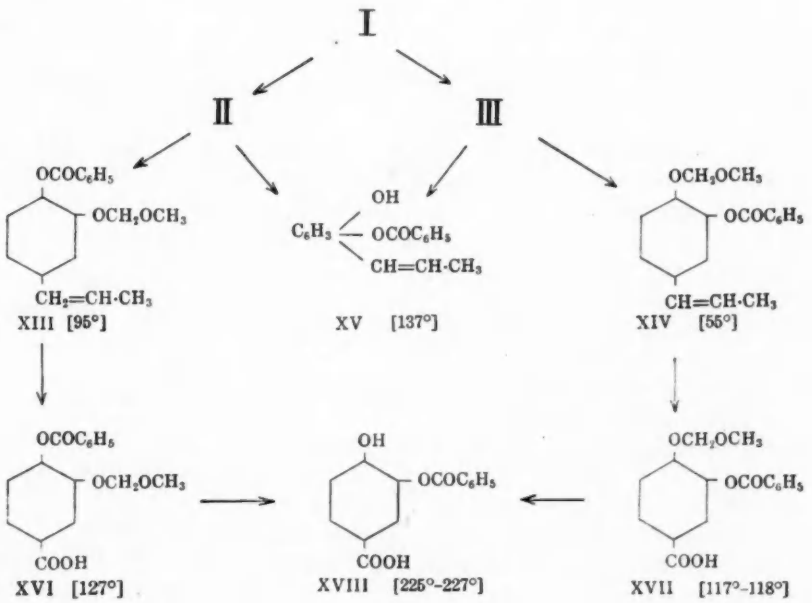
(3) *Ber.*, **51** (1918), 45.

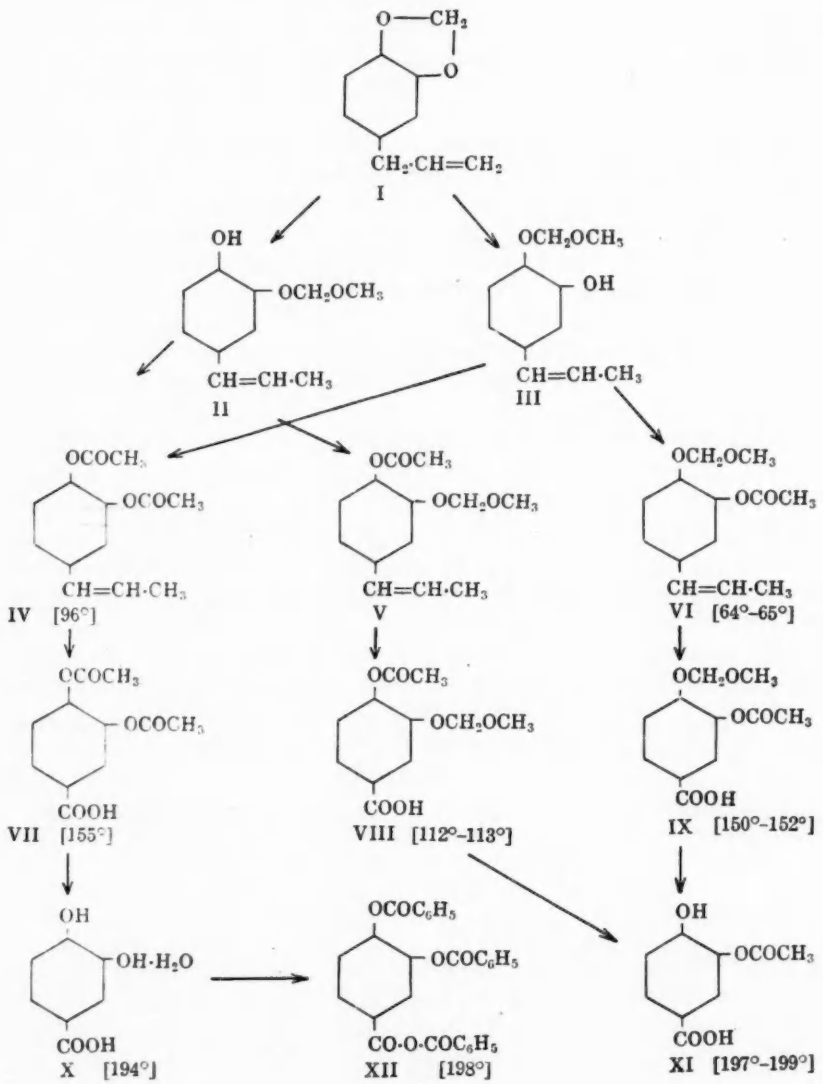


It is evident, therefore, that we have reached the same object of rearrangement by a method different from that of E. Fischer.



The above results are summarized as follows:




O—CH2
O
CH2·CH=CH2
I
OH
OCH2OCH3
CH=CH·CH3
II
OCH2OCH3
OH
CH=CH·CH3
III
OCOCH3
OCOCH3
CH=CH·CH3
IV [96°]
OCOCH3
OCH2OCH3
CH=CH·CH3
V
OCH2OCH3
OCOCH3
CH=CH·CH3
VI [64°–65°]
OCOCH3
OCOCH3
COOH
VII [155°]
OCOCH3
OCH2OCH3
COOH
VIII [112°–113°]
OCH2OCH3
OCOCH3
COOH
IX [150°–152°]
OH
OH·H2O
COOH
X [194°]
OCOC6H5
OCOC6H5
CO·O·COC6H5
XII [198°]
OH
OCOCH3
COOH
XI [197°–199°]

Experimental Part.

(1) **Decomposition of Safrol.** Potassium hydroxide (17 g.) was dissolved in 30 g. of methanol and transferred to the autoclave with 30 g. of safrol, and the mixture was kept at 200°–208° for three hours in an oil bath and then allowed to cool. The contents were poured out into water and the isomerized product, isosafrol, was extracted with ether. On distilling off the ether, 3 g. of isosafrol was obtained. The aqueous layer was cooled with ice and acidified with 110% of the theoretical amount of dilute sulphuric acid. The phenolic substance which floated out was extracted with ether. By distilling off the ether, 31 g. of the raw product was obtained which gave by redistillation 27 g. of the mixture of II and III.

(2) **Acetylation.** (A) *Preparation of the di-acetate.* (a) The decomposition product (100 g.) of safrol and acetic anhydride (105 g.) were kept at 140–145° on an oil bath for 3 hours. Water (150 c.c.) was added and the whole was warmed for 30 minutes on the water bath. On cooling, di-acetate separated out in crystals.

(b) The decomposed phenolic substance (40 g.) was dissolved in 40 g. of xylene, 24 g. of acetic anhydride and one drop of concentrated sulphuric acid were added, and the whole was heated under reflux condenser for two hours. The contents were poured into water, warmed on the water bath for 30 minutes, and cooled. The crystals thus separated were recrystallized from alcohol and showed the m.p. 95°. Yield was 24 g.

(B) *Preparation of the mono-acetates.* (a) The decomposed phenolic substance (100 g.), anhydrous sodium acetate (100 g.), and acetic anhydride (400 g.) were heated under a reflux condenser for 3.5 hours. The contents were poured into a double volume of water, warmed for one hour on the water bath, and then extracted with benzene. On distilling off the benzene, an oily substance was obtained which was subjected to fractional distillation under a reduced pressure of 14 mm.

Fraction	Temperature	Quantity distilled	d_{18}	n_{15}
1	–170°	5 g.		
2	170–172°	105 g.	1.1114	1.5383
3	172–176°	12 g.		

Molecular refraction of fraction 2 was found 66.0, the calculated value for $C_{13}H_{16}O_4$ being 63.05, and hence $J = 3.05$. As the similar derivatives of propenyl-benzene always show $J = 2-3$, the figures thus obtained seem to correspond to those of monoacetyl compound. Fraction 2 (90 g.) was changed to a soft lump by treating with the freezing mixture according to Kuwata.

On filtration by suction, it was separated into 25 g. (27.8%) of crystals (VI) and 65 g. (71.2%) of an oily matter (V). The crystals melted, after washed with cooled alcohol, at 64°.

Fraction	Temperature	Quantity
1	xylene	
2	–165°	2g.
3	165–167°	23.5g.
4	167–170°	0.5g.
5	170–171°	13.2g.

(b) The decomposed phenolic substance (50 g.), xylene (50 g.), and acetic anhydride (28 g.) were heated under a reflux condenser for 1.5 hours. The product was warmed with water for 30 minutes. The floating oily matter was fractionated under 13 mm. pressure. The fraction 2 gave a beautiful green coloration with $FeCl_3$ and proved to be the unchanged phenolic substance. The fraction 5 was the product aimed at and gave by freezing crystals melting at 64°.

(3) **Benzoylation.** The decomposition product of safrol (50 g.) was dissolved in KOH solution (15 g. in 250 c.c. of water); after adding benzoyl chloride (35 g.), the mixture was well stoppered and shaken for 3 hours. The soft lump formed was separated and treated with 150 c.c. of alcohol, from which 20 g. of crystals melting at 95° separated out. From the mother liquor allowed to stand for 3 days, there separated out 12 g. of crystals melting at 52°. The last filtrate was concentrated on the water bath to about 40 c.c. and allowed to stand when a third crop of crystals came out, which on recrystallization from alcohol melted at 137°.

(4) **Oxidation.** (a) *Protocatechuic acid di-acetate* (VII). Six grams of IV was mixed with 500 c.c. of water and 30 c.c. of 10% sulphuric acid and the mixture was subjected to oxidation by treating it on the water bath with a 2 per cent. solution of 20 g. of $KMnO_4$. The filtrate was salted out and then extracted with ether. After evaporation of ether 1.1 g. of white crystals were left behind, m.p. 142–150°. By repeating this process, 1.5 g. of crystals melting at 149° were obtained.

(b) *Methoxy-vanillic acid acetate* (VIII). Three grams of the oily part of the monoacetate described above was mixed with 300 c.c. of water and 20 c.c. of 10% sulphuric acid and the mixture was subjected to oxidation by adding 500 c.c. of water containing 10 g. of $KMnO_4$ on the water bath. After filtering and cooling, the product was treated exactly the same as in the case of the di-acetate mentioned above. The crystals obtained by recrystallizing twice from water melted at 112–113°. (Found: C, 54.7; H, 4.9; molecular weight (in camphor), 249.3. Calc. for $C_{11}H_{12}O_6$: C, 55.0; H, 5.0%; mol. wt., 240.)

(c) *Methoxy-isovanillic acid acetate* (IX). With the compound VI melting at 64°, the same treatment was repeated as in the case (b). The pure white crystalline product, after recrystallized three times from water, melted at 150-152°. (Found: C, 54.8; H, 5.1. Calc. for $C_{11}H_{12}O_6$: C, 55.0; H, 5.0%.)

(d) *Methoxy-isovanillic acid benzoate* (XVII). Two grams of the substance XIV melting at 55° was treated with 5 g.of $KMnO_4$ in 500 c.c. of water on the water bath as usual. Sulphuric acid was not added in this case, and the oxidation was found to be very slow. After warming for three hours on the water bath, a small quantity of methanol was added to reduce the remaining $KMnO_4$. The product was then filtered, acidified with acetic acid, and extracted with ether. The pure white needle crystals obtained by recrystallizing twice melted at 117-118°. (Found: C, 62.9; H, 5.1. Calc. for $C_{16}H_{14}O_6$: C, 63.6; H, 4.6%.)

(e) *Methoxy-vanillic acid benzoate* (XVI). With the compound XIII melting at 95°, exactly the same treatment as in the case (d) was carried out. The pure white crystals obtained by recrystallizing twice melted at 127°. (Found; C, 63.3; H, 4.8. Calc. for $C_{16}H_{14}O_6$: C, 63.6; H, 4.6%.)

(5) **Saponification and the Rearrangement of Acyl Group.** (a) *Protocatechuic acid* (X). The substance VII (1 g.) was heated with 10 c.c. of methanol and 1 c.c. of concentrated hydrochloric acid under the reflux condenser for 1.5 hours. Water (30 c.c.) was then added, methanol was distilled off, and the residue was extracted with ether. The solid matter left on evaporating off ether was recrystallized from water. It melted now at 195° and weighed 0.5 g. When mixed with a pure sample of protocatechuic acid there was no change of m.p., showing the completeness of saponification.

(b) *Rearrangement of the acyl group from VIII to XI.* The substance VIII (0.2 g.) melting at 112-113° was warmed with 3 c.c. of glacial acetic acid and one drop of concentrated hydrochloric acid on the water bath for an hour. Water is then added and the product was extracted with ether. The ethereal extract was washed with water; on evaporation of ether, the residue was twice recrystallized from water, yield 0.05 g. The substance melted at 198° and when mixed with protocatechuic acid, depression of the melting point resulted.

(c) *Partial saponification from IX to XI.* The substance IX (0.1 g.) was warmed with 3 c.c. of 30% alcohol and 2 drops of 10% sulphuric acid on the water bath for 3 hours. The reaction product was extracted with ether as usual. A small quantity of a substance melting at 198°

was obtained which did not lower the m.p. when mixed with the substance obtained in (b).

(d) *Rearrangement from XVI to XVIII and from XVII to XVIII.* The substance XVI (0.5 g.) was warmed with 5 c.c. of glacial acetic acid and 1 c.c. of concentrated hydrochloric acid on the water bath for 1.5 hours, when a rather strong resinification took place. The product was extracted as usual with ether and a small amount of a substance melting at 224° after recrystallized from water was obtained. Another substance with m.p. 225° was obtained from XVII on treating it exactly in the same manner. The two substances did not show any lowering of melting point when mixed together, showing that they are the same compound.

Addendum. *Dibenzoyloxy-benzoic acid benzoylester* (XII). Protocatechuic acid (1 g.) and NaOH (4 g.) were dissolved in 36 g. of water. Under ice cooling, 9.1 g. of benzoyl chloride was added and the whole was shaken, when a white substance separated copiously. It was collected with suction, and recrystallized four times with use of activated charcoal, m.p. 198°. (Found: C, 71.7; H, 3.4, molecular weight (in camphor), 449. Calc. for $C_{28}H_{18}O_7$: C, 72.1; H, 3.8%, mol. wt., 466.)

Research Laboratory of
Nippon Koryo Yakuhin Kaisha, Ltd., Kobe.

ON THE CATALYTIC ACTION OF ACTIVE CARBON UPON TERPENES AND THE RELATED COMPOUNDS.

By Seizo KIMURA.

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The investigations of Ruzicka and his co-workers[1] on the compounds of the higher terpene series with use of the dehydrogenation reaction of sulphur are too well known to need detailed statements. The present author has used active carbon together with sulphur in his studies and found that cyclic compounds of the terpene series can, in liquid phase, easily be transformed into aromatic compounds. This fact made him interested in the catalytic action of active carbon upon terpenes and the related compounds, so as to start an investigation on this reaction especially in the liquid phase.

(1) *Helvetica Chim. Acta*, **4** (1921), 505.

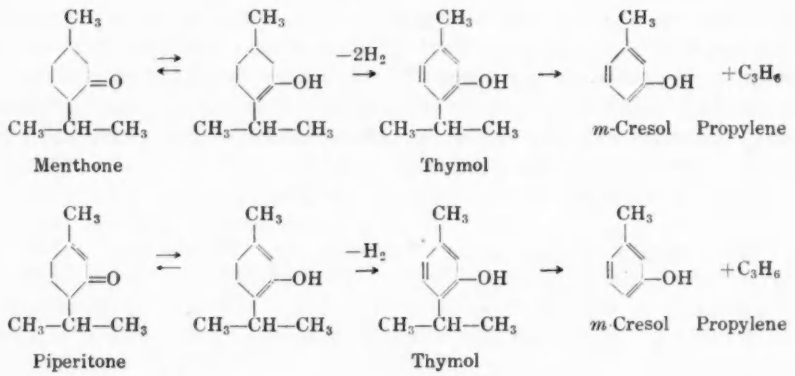
The studies of catalytic action of active carbon have been made by various workers and some of the results have been already applied in industry. Most of them were, however, made by the reaction in the gaseous phase and up to 1932 there was none made upon the compounds of terpene series, except that of Asahina and Nakanishi[2] who reported the fact that cineol is converted to *p*-cymene by the action of palladium-charcoal or charcoal for bleaching purpose. The present author has also made investigations, in relation to the dehydrogenation reaction of sulphur, upon the action of active carbon alone on cineol. He then found a small quantity of *p*-cymene as the dehydration and dehydrogenation product of cineol.

(I) Catalytic Action upon Menthone and Piperitone. As active carbon exerts dehydrogenation action, it is expected to cause upon the terpene-ketones capable of existing in the enol form, such as menthone and piperitone, simultaneously a dehydrogenation action and a keto-enol metamerization. *l*-Menthone (b.p. 72°C./6 mm., $d_4^{25.5}$ 0.8905, n_D^{20} 1.4513, $[\alpha]_D^{20}$ −24.75) (50 g.) made by oxidation of menthol by Beckmann's method was heated with 25 g. of active carbon under a reflux condenser for 20 hours, the internal temperature being kept at 220°C. From the resulting oily material, about 2.7–3.4 g. of a phenolic substance was extracted with 5% NaOH solution. In this latter substance *m*-cresol was identified by elementary analysis and also by conversion into trinitro-*m*-cresol (m.p. 105–106°C.). A small quantity of thymol was also identified as thymol phenylurethane (m.p. 106–107°C.). The residue after the removal of the phenolic substance consisted of unacted menthone and it was noticed that during this reaction there was an optical transformation of *l*-menthone into *d*-menthone.

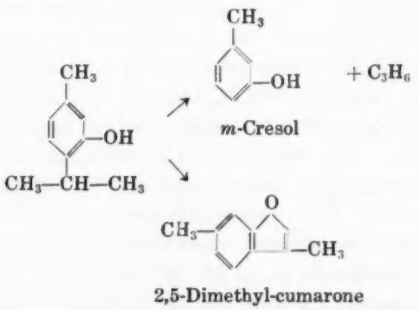
Piperitone (b.p. 90.5–92°C./5 mm., d_4^{24} 0.9305, $n_D^{26.8}$ 1.4831, $[\alpha]_D$ −48.22) (50 g.) prepared by refining oil of *Eucalyptus dives* of Australian origin was heated with 25 g. of active carbon for 20 hours, the internal temperature being kept at 200–240°. About 13.4 g. of a phenolic substance was extracted from the reaction product by treating it with 5% NaOH solution. As before, in this phenolic substance, *m*-cresol was identified by the elementary analysis and conversion into trinitro-*m*-cresol (m.p. 105–106°C.), and a small quantity of thymol was recognized by the elementary analysis and conversion into thymol phenylurethane (m.p. 106–107°C.). The residue after separating the phenolic substance consisted chiefly of the unacted piperitone which was identified by preparing α- and β-semicarbazones (m.p. 226–227° and 174–176° respectively). As expected, the keto-enol metamerization took place by which the enol form of menthone or piperitone was first formed. By their

(2) *J. Pharm. Soc. Japan*, **52** (1928), 1.

dehydrogenation, thymol was then produced from which the isopropyl group was split off to form *m*-cresol as represented in the following scheme :



In order to make the final mechanism clear, 50 g. of thymol (m.p. 50–51°C.) was mixed with 25 g. of active carbon and subjected to the same treatment as before by which about 7.3 g. of a phenolic substance was obtained. This latter substance was proved by elementary analysis and by the formation of trinitro-*m*-cresol to be chiefly *m*-cresol itself. It was interesting here to find that about 5.4 g. of a neutral substance was obtained which was identified as 2,5-dimethylcumarone by the physical constants of its principal distillate (b.p. 212–217°C., $d_4^{25.5}$ 1.0352, $n_D^{22.5}$ 1.5521), molecular refraction (found : 44.66–44.99, theoretical : 43.76 for $C_{10}H_{10}O$), colour reaction, elementary analysis, and the formation of its picrate (m.p. 75–76°C.). In this way, thymol is changed to *m*-cresol by splitting off of the isopropyl group by the action of active carbon. At the same time it undergoes dehydrogenation and is changed into a compound of cumarone series. This is represented by the following scheme :



This formation of dimethylcumarone is presumed to take place also when menthone or piperitone is acted upon by active carbon ; though its identification is expected to be impossible on account of a too small trace of it present.

(II) Catalytic Action upon Cyclic Terpene Alcohols. From the resemblance of the properties of active carbon with those of acid clay, Florida earth, etc., it is inferred that it will also exert a dehydration action upon terpene alcohols. For examining the action of active carbon, *d*- and *l*-terpineol were taken as representative members of cyclic tertiary terpenealcohols. *d*-*α*-Terpineol (m.p. 35°C., d_4^{15} 0.9390, n_D^{14} 1.4843, $[\alpha]_D^{25}$ +9.85) (100 g.) made by refining pine oil of the American origin was heated with 20 g. of active carbon for 5 hours at about 200°C. About 67.9 g. of an oily product and 9.8 g. of water were obtained. By repeated refining of the oil, it was proved by the physical constants, molecular refraction, elementary analysis, and by the formation of dipentene-tetrabromide (m.p. 124°C.) that it consisted almost entirely of dipentene.

By the action of boric acid upon brown comphor oil, after the removal of safrol, an alcoholic substance was obtained which was separated as boric acid ester. By refining the latter product, *l*-*α*-terpineol (m.p. 35°C., $d_4^{24.8}$ 0.9323, n_D^{25} 1.4802, $[\alpha]_D^{25}$ −13.70) was prepared. This substance (25 g.) was mixed with 5 g. of active carbon and heated for 6 hours at about 200°C. About 19.6 g. of an oily product and 4.3 g. of water were obtained. In this oil, dipentene was also identified.

Active carbon was also made to act upon *l*-menthol and *d*-borneol as representative of cyclic secondary terpene alcohols.

l-Menthol (m.p. 42–43°C., $[\alpha]_D^{12}$ −49.07 in alcoholic solution) (50 g.) was heated with 10 g. of active carbon for 5 hours at 200°C. An oily distillate (16.9 g.) and 3.6 g. of water were obtained. The principal distillate was shown to be Δ^3-*p*-menthene by its physical constants (b.p. 166-167°C., d_4^{12} 0.8108, n_D^{22} 1.4532, $[\alpha]_D^{21}$ +15.22), molecular refraction (Found: 45.958, theoretical: 45.713 for $C_{10}H_{18}\overline{1}$), and elementary analysis. The dextro-rotatory property of this substance is especially to be noted. The residual part in the flask was extracted with ether and proved to be unchanged *l*-menthol.

d-Borneol (m.p. 203–204°C.) (50 g.) was heated with active carbon (50 g.) for 4 hours over direct flame. On distilling, 31.4 g. of an oil and 6 g. of water were obtained. By repeated distillation, the principal distillate was found to correspond well to camphene in its physical constants (b.p. 158–161°C., d_4^{15} 0.8651, $n_D^{22.5}$ 1.4685), molecular refraction (found: 44.025, calculated for $C_{10}H_{16}\overline{1}$: 43.513), and the results of elementary analysis. The trial to separate a crystalline sample of camphene from this material by cooling was rewarded only with a minimum quantity of crystals melting at 49°C. and with a camphor-like odour.

Judging from these experimental results, the dehydration activity of active carbon resembles that of acid clay though it is not so violent as

the latter. With acid clay, the action is quickly completed in 20–30 minutes, while with active carbon it proceeds slowly and at a rather high temperature.

(III) Catalytic Action upon Acyclic Terpene Alcohols. Upon the presumption that the action of active carbon must be the same on acyclic compounds as on cyclic compounds, its reaction was studied upon geraniol and linalool representing cyclic terpene-alcohol compounds.

Geraniol to be used was separated and refined from citronella oil of the Javanese origin and had d_4^{15} 0.8807, n_D^{17} 1.4769, and $[\alpha]_D^{15}$ ±0. It (200 g.) was heated with 40 g. of active carbon for 21 hours at 225°C. About 130 g. of an oily matter and 16.1 g. of water were obtained. By repeated distillation, the lower boiling portion (b.p. below 70°C./8 mm.) yielded myrcene which was identified by its physical constants (b.p. 47–49°C./7.5 mm., d_4^{15} 0.8062–0.8081, n_D^{15} 1.4667–1.4692, $[\alpha]_D^{16}$ ±0), molecular refraction (found: 46.846–46.982, calculated for $C_{10}H_{16}\overline{3}$: 46.979), and the results of elementary analysis. Besides myrcene thus identified, there was also found dipentene recognizable by conversion into its tetrabromide. The portion of the intermediate boiling points (b.p. 100–110°C./8 mm.) consisted chiefly of the unchanged geraniol. When the latter was removed, the residue showed physical constants well approaching those of linalool. The higher boiling portion (b.p. above 110°C./8 mm.) was repeatedly distilled, but it gave nothing worth of being considered as the chief constituent. However, it is presumed to have been oxides of the diterpene series.

Linalool prepared by refining the linalool of bois de rose, had the constants: b.p. 74°C./5.5 mm., d_4^{23} 0.8687, $n_D^{23.5}$ 1.4590, $[\alpha]_D^{24}$ −14.18. It (300 g.) was mixed with 60 g. of active carbon and subjected to the same procedure as before. An oily product weighing 159.7 g. was obtained together with 29.6 g. of water. The oily matter gave by repeated fractional distillation a lower boiling portion (b.p. below 70°C./7 mm.) which yielded as the chief constituent dipentene (tetrabromide m.p. 124°C.) besides a small quantity of a substance corresponding to myrcene (b.p. 43–44°C./5.5 mm., d_4^{20} 0.8087, n_D^{20} 1.4671). The portion of the intermediate boiling points (b.p. 70–85°C./7 mm.) consisted chiefly of the unchanged linalool. The higher boiling portion (b.p. above 85°C./7 mm.) gave a compound showing physical constants (b.p. 150–155°C./5 mm., d_4^{18} 0.8858, n_D^{17} 1.5014), molecular refraction (found: 90.467, calculated for $C_{20}H_{32}\overline{4}$: 90.484), and the results of elementary analysis well agreeing with those of α-camphorene, which was synthesized by Semmler and Jonas[3] from myrcene and had the constants: b.p. 178–180°C./8.5 mm.,

(3) *Ber.*, **46** (1913), 1566.

d_{18} 0.8844, n_D 1.50199, $[\alpha]_D$ ±0. This must have been formed by polymerization of myrcene produced by dehydration of linalool.

The attempt to detect geraniol in the distillates was made in vain.

From the above-given results, it is positively ascertained that active carbon exerts a power of dehydration, of ring formation, and of polymerization upon acyclic terpene alcohol compounds like geraniol and linalool.

(IV) Catalytic Action upon Acyclic Terpene Aldehydes. Citral and citronellal were taken as representatives of acyclic terpene aldehydes upon which the action of active carbon was tested.

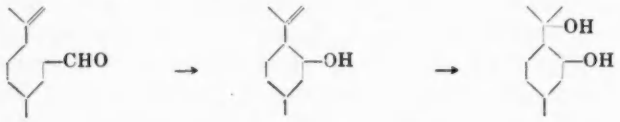
Citral was separated from lemongrass oil of the Indian origin and showed the constants: b.p. 96–97°C./6.5 mm., d_4^{15} 0.8918, n_D^{20} 1.4872, $[\alpha]_D^{10}$ ±0. It (200 g.) was mixed with 40 g. of active carbon and slowly heated in an oil-bath with constant stirring. At about 135°C. the reaction became very brisk. The yield of the oily reaction product was about 50% of the citral used. By repeated fractional distillation a lower fraction was obtained which proved to be *p*-cymene by its physical constants (b.p. 174–177°C., d_4^{15} 0.8593–0.8624, n_D^{20} 1.4912–1.4940), molecular refraction (found: 45.390–45.445, calculated for $C_{10}H_{14}$: 44.845), the results of elementary analysis, and the property of forming *p*-oxyisopropyl-benzoic acid (m.p. 155–156°C.). The higher boiling fraction (b.p. 160–165°C./4 mm., d_4^{15} 0.9379, n_D^{20} 1.5251) showed in elementary analysis the presence of a hydrocarbon of the molecular formula $C_{20}H_{28}$. Besides, the presence of a small quantity of a terpene was inferred, which resembled citral-terpene detected by Horiuchi[4] among the reaction products obtained by the action of 20% sulphuric acid upon citral.

Citronellal (b.p. 69–71°C./5 mm., d_4^{15} 0.8553, n_D^{20} 1.4467, $[\alpha]_D^{10}$ +11.02) was obtained by refining citronella oil of the Javanese origin. It (300 g.) was mixed with 60 g. of active carbon and subjected to the treatment as before. When the temperature of the oil bath reached about 99°C., a brisk reaction commenced, and the yield of the oily reaction product was about 57% of the citronellal taken. Upon fractional distillation, about 45 g. of a distillate having properties of isopulegol was obtained. After repeated purification by distillation, it showed physical constants (b.p. 66-68°C./4 mm., d_4^{15} 0.9148, n_D^{20} 1.4704, $[\alpha]_D$ +2.15), molecular refraction (found: 47.209, calculated for $C_{10}H_{18}O$: 47.238), and the results of elementary analysis proving it was isopulegol. By oxidation with the chromic acid mixture, it formed isopulegone which was converted to the oxime (m.p. 122–123°C.).

(4) *Mem. Coll. Sci., Kyoto Imp. Univ.*, **11** (1928), 190.

The higher boiling fraction had as the chief constituent di-isopulegol ether (b.p. 160–170°C./4 mm.) showing upon a further purification the physical constants (b.p. 157–158°C./4 mm., d_4^{15} 0.9188, n_D^{20} 1.4819, $[\alpha]_D^{13}$ −0.87), and the results of elementary analysis corresponding to the formula $C_2H_{34}O$. Besides this, a very small quantity of a terpene hydrocarbon was detected with the constants: b.p. 47–55°C./4 mm., d_4^{15} 0.8594, n_D^{20} 1.4826, $[\alpha]_D$ +39.92.

It was thus recognized that active carbon possesses dehydration activity as well as the action of ring formation and polymerization upon acyclic terpenealdehyde compounds. Especially interesting was the fact that isopulegol was very easily formed from citronellal without use of any solvent. This fact makes the present author concur to the view[5] that isopulegol is formed by the direct ring formation of citronellal:



In order to corroborate this view, the temperature of the oil bath was kept comparatively low at about 70°C. to avoid the formation of water by the decomposition of citronellal. After a slow reaction taking place during three hours, there was found a large quantity (about 22%) of isopulegol formed which could not be thought as having come through the stage of menthoglycol.

(V) Catalytic Action upon Safrol and Isosafrol. Under the expectation that safrol and isosafrol would undergo the opening of their methylene-dioxy ring by active carbon, the reaction was tried under pressure, as it was known by experiments not to take place under ordinary pressure.

Safrol was prepared by separation and purification from brown camphor oil (b.p. 232.5–233°C., d_{15} 1.1050, n_D^{20} 1.5378, $[\alpha]_D$ ±0). It (200 g.) was mixed with 40 g. of active carbon and slowly heated in an autoclave. At about 190°C., a brisk reaction commenced to taken place showing a pressure of 40 atmospheres and rising in temperature to 265°C. The reaction product was extracted with ether and the dark brownish oily matter was subjected to distillation under reduced pressure, when 40.3 g. of an oil was obtained. At the same time an increase of coaly matter was noted. The chief constituent consisting of about 22 g. of phenolic material had the properties (b.p. 118–130°C./4 mm., d_4^{15} 1.0942–1.0946, n_D^{20} 1.5441–1.5444), from

(5) *Loc. cit.*; *J. Soc. Chem. Ind., Japan*, **34** (1931), 161.

which and from the result of elementary analysis there was attributed to it a formula $C_9H_{12}O_2$ containing two hydroxyl groups and no methoxyl group. To prove the constitution of the product, it was methylated in usual way when it showed physical constants: b.p. 95–100°C./4 mm. d_4^{15} 1.0167, n_D^{20} 1.5164. From this and from the results of elementary analysis and determination of methoxyl groups, the methylated oil was proved to have the molecular formula $C_{11}H_{16}O_2$ containing two methoxyl groups. It is clear then that the phenolic substance corresponding to it contains two hydroxyl groups.

The methylated oil gave on oxidation with potassium permanganate veratric acid (m.p. 179–181°C.). By nitration, it gave 6-nitro-3,4-dimethoxy-1-propyl-benzene (m.p. 80.5–81°C.).[6] These results show that the methylated oil is 3,4-dimethoxy-1-propyl-benzene and that the chief constituent of the higher boiling fraction of the phenolic matter produced from safrol is 3,4-dihydroxy-1-propyl-benzene. The 3,4-dihydroxy-1-propyl-benzene obtained by the present author was an difficultly crystallizable oil, so that it perhaps contained some impurities.

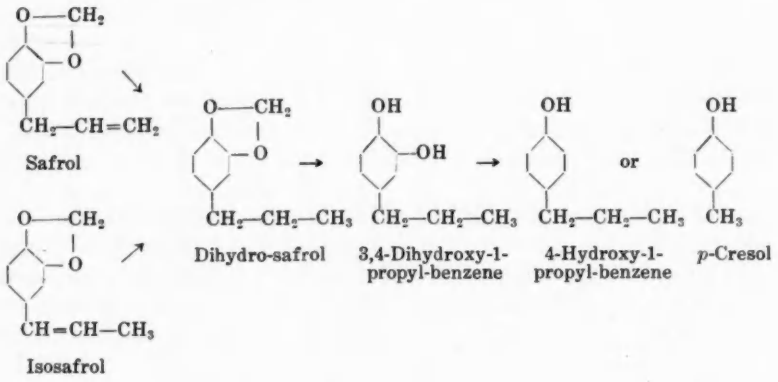
Another sample of 3,4-dimethoxy-1-propyl-benzene (b.p. 110–115°C./3 mm., d_4^{15} 1.0569, n_D^{20} 1.5652) was prepared by reduction of methyl-iso-eugenol with absolute alcohol and metallic sodium. The 6-nitro-3,4-dimethoxy-1-propyl-benzene (m.p. 80.5–81°C.) prepared by its nitration showed no change of melting point when mixed with the nitration product mentioned above. From the phenolic matter obtained as above, a small quantity of a substance of comparatively low boiling point (b.p. 85–115°C./5 mm., d_4^{26} 1.0266–1.0340, n_D^{26} 1.5291–1.5285) was obtained. When methylated, it gave an oil having physical constants: b.p. 65–70°C./4.8 mm., d_4^{15} 0.9809, n_D^{20} 1.5129. From the results of elementary analysis and from the fact that by oxidation it gave anisic acid (m.p. 179–181.5°C.), the methylated oil was found to be *p*-cresol-methyl-ether and the original phenolic matter was inferred to be *p*-cresol, although the formation of 4-hydroxy-1-propyl-benzene is not precluded. The material was too small in quantity to decide the question definitely.

The neutral material obtained had physical constants: b.p. 80–84°C./3.5 mm., d_4^{28} 1.0786–1.0768, n_D^{28} 1.5282–1.5255. It is quite different from safrol or isosafrol. From the fact that the phenolic substance contained a propyl group and that dihydro-safrol can be obtained in a large quantity from isosafrol, the formation of dihydrosafrol from safrol can be easily imagined, and the neutral substance mentioned above is safely presumed to be a mixture of safrol and dihydro-safrol.

A sample of isosafrol (b.p. 114–117°C./7 mm., d_{15} 1.1247, n_D^{20} 1.5757, $[\alpha]_D$ ±0) was obtained by isomerization of safrol in the usual way. It (200 g.)

(6) H. Thoms, *Ber.*, **36** (1903), 860.

was heated with 40 g. of active carbon as before under pressure. At 198°C. the reaction began to take place very briskly and the pressure rose to 33 atmospheres with the rise of temperature to 284°C. At the completion of the reaction, 37.8 g. of an oily matter was distilled off at 61–125°C. under 4 mm. In about 10 g. of phenolic substance from the oily reaction product, 3,4-dihydroxy-1-propyl-benzene was identified as in the case of the experiment with safrol. The neutral substance was identified as almost pure dihydro-safrol from the physical constants (b.p. 80–83°C./4 mm., d_4^{29} 1.0626, n_D^{30} 1.5151), and the molecular refraction (found : 46.54, calculated for $C_{10}H_{12}O_2$: 45.87), and the results of elementary analysis. From these results it is inferred that, by heating safrol and isosafrol with active carbon, the reaction runs in such a way that a portion is decomposed and carbonised producing hydrogen which is added to the double bonds of the allyl or propenyl group, changing it to a propyl group. At the same time the methylene-dioxy ring is split, chiefly to produce dihydroxy compounds, a small fraction of which is converted to hydroxy compounds by the loss of one hydroxyl group. This is made clear by the following scheme :



While in the experiments with safrol the neutral substance consists of a mixture of unchanged safrol and dihydro-safrol, in the case of isosafrol it consists almost wholly of dihydro-safrol. This is easily understood from the consideration that, generally in the reduction with metallic sodium and alcohol, the propenyl group is more easily hydrogenated than the allyl group.[7] The fact that carbon is liberated at the same time with the liberation of hydrogen

(7) G. Ciamician and P. Si ber, *Ber.*, **23** (1890), 1162; A. Klages, *Ber.*, **32** (1899), 1439.

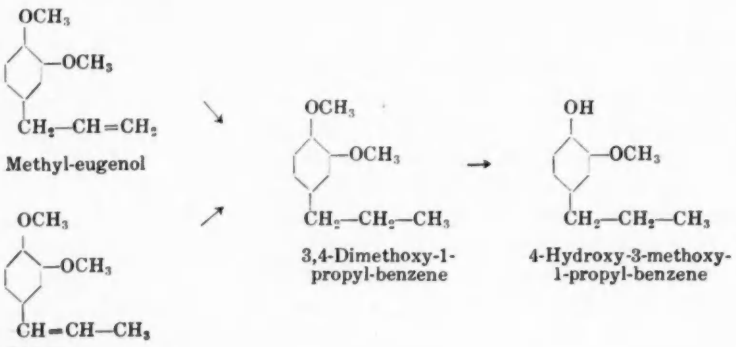
by the decomposition of the material, is made clear by the existence of a much larger quantity of carbon at the end of reaction than at the beginning.

From the results reported here it is concluded that active carbon exerts a splitting action upon the methylene-dioxy ring of safrol and isosafrol as well as the catalytic hydrogenation action.

VI. Catalytic Action upon Methyl-eugenol and Methyl-isoeugenol. From the above-mentioned experiments it was expected that active carbon may have a de-methylating action upon the methoxyl group. As it was also desired to extend the catalytic hydrogenation experiment to other kinds of compounds, the present author tested the activity of active carbon upon methyl-eugenol and methyl-isoeugenol. A sample of methyl-isoeugenol (b.p. 125–131°C./6 mm., $d_4^{18.8}$ 1.0590, $n_D^{18.5}$ 1.5707) was obtained by methylating isochavibetol and purifying the product in the usual way. It (200 g.) was mixed with 40 g. of active carbon and slowly heated in an autoclave up to 247°C., when a brisk reaction commenced raising the pressure to 24 atmospheres. At the completion of the reaction, the product was extracted with ether. The small quantity of the phenolic substance contained in the oily product showed physical constants (b.p. 90–93°C./4.5 mm., $d_4^{21.5}$ 1.0487, $n_D^{22.2}$ 1.5239), colour reactions, and results of elementary analysis proving that it consisted of 4-hydroxy-3-methoxy-1-propyl-benzene. The main fraction (about 20 g.) of the neutral matter was subjected to repeated fractionation and showed the physical constants: b.p. 108–110°C./6 mm., $d_4^{19.2}$ 1.0140, n_D^{21} 1.5159. From these figures and from the results of elementary analysis, it was identified as 3,4-dimethoxy-1-propyl-benzene. This conclusion was corroborated by further facts that it produces by oxidation with potassium permanganate veratric acid (m.p. 179–181°C.) and that it yields by nitration 6-nitro-3,4-dimethoxy-1-propyl-benzene.

A sample of methyl-eugenol (b.p. 123°C./9 mm., d_4^{17} 1.0372, $n_D^{17.8}$ 1.5337) was prepared by methylation of eugenol. It (200 g.) was heated with 40 g. of active carbon under pressure as before. From the reaction product, a small quantity of phenolic substance and a large amount of neutral substance were obtained. The main fraction of the neutral material was shown by the elementary analysis and by the nitration to 6-nitro-3,4-dimethoxy-1-propyl-benzene to consist chiefly of 3,4-dimethoxy-1-propyl-benzene. The physical constants (b.p. 110-112°C./6 mm., $d_4^{16.4}$ 1.0184, n_D^{6} 1.5208) did not, however, agree with those obtained before for the product from methyl-isoeugenol: this is due perhaps to the admixture of the unchanged material. This is again due to the different susceptibilities to hydrogenation of allyl group and propenyl group, endorsing the conclusion already drawn by the author in the case of safrol and isosafrol.

The reaction mechanism inferred from the above results is as follows. The hydrogen produced by thermal decomposition under pressure is added to the double bonds of allyl and propenyl groups by the catalytic action of active carbon to change them to a propyl group. The hydroxy compounds are then formed by de-methylation. Active carbon thus exerts a catalytic hydrogenation as well as de-methylation as in the previous instances. This is schematized as follows:



Cantelo[8] has made investigations of catalysis by animal charcoal, silica gel, etc., upon the thermal decomposition of methane. Kusama and Uno[9] have subjected methane to thermal decomposition under the catalysis of nickel with the formation of carbon and hydrogen. The latter concluded that the relation between the quantity of the catalyser and the percentage of the hydrogen formed depended upon the catalytic activity of carbon which accumulated in the reaction. In the experiments reported here, active carbon is considered to have exerted some catalytic activity of thermal decomposition.

The investigation here described was performed under the kind guidance of Dr. Kashichi Ono to whom a sincere acknowledgment is herewith rendered by the author.

Research Laboratory of
Nippon Koryo Yakuhin Kaisha, Ltd.,
Kobe.

(8) *J. Phys. Chem.*, **28** (1924), 1036.
(9) *Sci. Pap. Inst. Phys. Chem. Research, Japan*, **8** (1929), 1.

DETERMINATION OF SILICIC ACID BY VOLUMETRIC METHOD.

By Sansei KITAJIMA.

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Determination of silicic acid has hitherto been executed by making in usual ways a solution of the sample to be analysed, by evaporating the solution with hydrochloric or nitric acid, and by weighing the resulting silicon dioxide. In the determination of a minute quantity of the same, the yellow colour of ammonium silicomolybdate is conveniently utilized by comparing it with the colour of a standard solution having the same constituents and containing a known quantity of silicon.(1) Ammonium silicomolybdate can be prepared from an acetic or a sulphuric acid solution of silicate and a solution of ammonium molybdate. In case the comparison of the two colours is unfavourable and does not give accurate results, a solution of benzidine or stannous chloride is added to the yellow solution of the ammonium silicomolybdate and the resulting colour of benzidine blue or molybdenum blue is used for the comparison, so that the determination of a very minute quantity of silicic acid can be made readily.

The yellow compound described above appears usually in solution when acid solutions of ammonium molybdate and silicate are mixed together. With a view to arriving at an easy and accurate method of determination of silicic acid, experiments have been made by the present author to see whether or not this compound can be separated in the form of a precipitate containing all of silicic acid present in the original solution. They have shown that silicic acid can be separated in the form of precipitate by a method which has not been used up to now, and that the same acid can be determined by a volumetric method. A detailed account on this subject being expected to be issued from The Institute of Physical and Chemical Research, Tokyo, outlines only are here presented.

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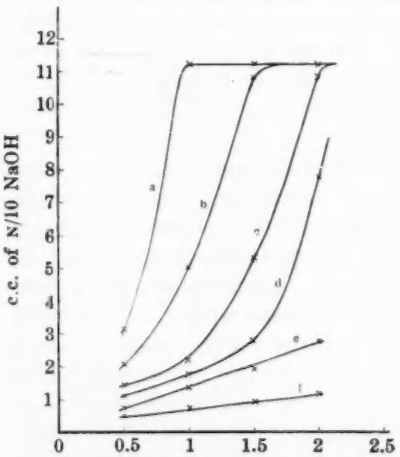
(1) F. Diénert and F. Wandenbulcke, *Compt. rend.*, **176** (1923), 1478; *Bull. soc. chim.*, [4], **34** (1923), 1131. Atkins and Wilson, *Biochem. J.*, **20** (1923), 1223. Isaac, *Bull. soc. chim. biol.*, **6** (1924), 157. Foulger, *J. Am. Chem. Soc.*, **49** (1927), 429. F. J. King and C. C. Lucas, *J. Am. Chem. Soc.*, **50** (1928), 2395. Oberhanser and Schormüller, *Z. anorg. allgem. Chem.*, **178** (1929), 381. F. Feigl und P. Krumholz, *Ber.*, **62** (1929), 1138. F. Feigl, *Z. anal. Chem.*, **77** (1929), 299. W. F. Hillebrand and G. E. F. Lundall, "Applied Inorg. Analysis," (1929), 540. F. Feigl, "Qualitative Analyse mit Hilfe von Tüpfelreaktion," (1931), 310.

The present author has once made studies on the suitable conditions for the complete precipitation of ammonium phosphomolybdate, and found that the concentration of nitric acid, ammonium nitrate, and ammonium molybdate had important effects on the precipitation.[2] In the same manner, he has

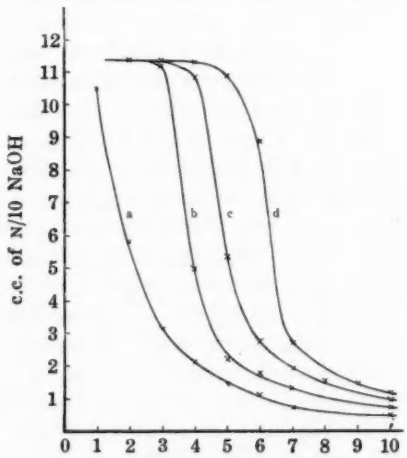
Table 1.

Quantity (g.) of ammonium nitrate added	Quantity (c.c.) of N/10 NaOH solution required for the titration of the yellow precipitate		
	When 3 c.c. of HNO_3 and 1 c.c. of the ammonium molybdate solution were used	When 4 c.c. of HNO_3 and 1 c.c. of the ammonium molybdate solution were used	When 5 c.c. of HNO_3 and 1.5 c.c. of the ammonium molybdate solution were used
0	0	0	0
1	0	0	0
3	10.15	4.48	4.36
5	11.31	5.05	6.37



a: NH_4NO_3 5 g., HNO_3 3 c.c.
b: „ „ „ 4 „
c: „ „ „ 5 „
d: „ „ „ 6 „
e: „ „ „ 7 „
f: „ „ „ 10 „

Fig. 1.



a: NH_4NO_3 5 g., Ammonium molybdate sol., 0.5 c.c.
b: „ „ „ 1.0 „
c: „ „ „ 1.5 „
d: „ „ „ 2.0 „

Fig. 2.

(2) S. Kitajima, *Sci. Pap. Inst. Phys. Chem. Research, Japan*, **16** (1931) 285; *Bull. Inst. Phys. Chem. Research, Japan*, **10** (1931), 65.

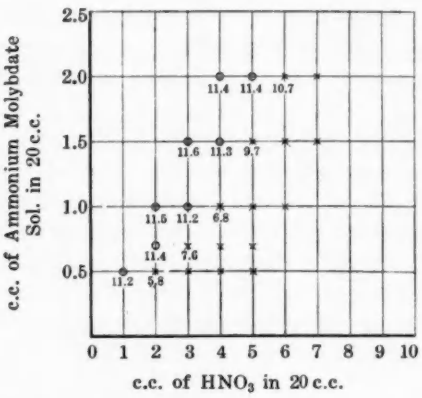
recently found that the increase in the concentration of ammonium nitrate and molybdate decreases the solubility of the yellow precipitate of ammonium silicomolybdate, and that when the concentration of nitric acid is increased within a certain limit, the solubility of the yellow precipitate is increased, but when the concentration of the same is increased beyond the same limit, silicic acid tends to separate itself and not to form the yellow precipitate, so that the determination of silicic acid becomes impossible. An example showing the conditions for the precipitation is given in Table 1 and Figs. 1 and 2.

Reagents employed in the experiments were as follows: nitric acid sp. gr. 1.379, about 13.4 N; ammonium nitrate solution contained 1 g. of the repeatedly recrystallized salt in 1.5 c.c. of the solution; ammonium molybdate solution contained 0.232 g. of molybdenum in 1 c.c. and was made by dissolving 50 g. of the salt in 100 c.c. of dilute ammonia solution obtained from 1 volume of concentrated ammonia (sp. gr. 0.9) and 3 volumes of water. The sodium silicate solution was made by dissolving about 1% anhydrous sodium silicate and confirmed by gravimetric method to contain 0.0622 g. of SiO_2 in 10 c.c.

Various quantities of the sodium silicate solution, water, the ammonium molybdate solution, the nitric acid, and the ammonium nitrate solution were taken in succession into an Erlenmeyer flask having a glass stopper, so as to make the total volume of the mixture just 20 c.c. The mixture was shaken and allowed to stand in a bath of about 70° for one hour. The yellow precipitate was collected, washed, and titrated with N/10 NaOH solution, phenolphthalein being employed as indicator. In the filtration and washing, various sorts of filters were employed, and the precipitate was found to be liable to come more or less into the washings, in every case where filter paper was used. Glass filters having fine pores were found to be most suitable for washing. Aqueous solutions of nitric acid, potassium nitrate, ammonium nitrate, and other salts in varying concentrations were separately employed in washing the precipitate in order to avoid its passing through the filter without success. A solution of 15% NH_4NO_3 and 0.02% HNO_3 (about 0.00027 N in HNO_3) was finally found to be most suitable for the washing purpose.

Various known quantities of the sodium silicate solution were taken, and silicic acid was precipitated as yellow ammonium silicomolybdate by the method described above by using varying quantities of the reagents. The precipitates were titrated with a standard NaOH solution. Among various values obtained by the titration, there were found a number of the largest

and identical ones. Out of these values and those showing the concentrations of the reagents in the solutions, in which the yellow precipitates formed, a diagram shown in Fig. 3 has been made, which shows the interdependence of the reagents in the complete precipitation of silicic acid.



The diagram in Fig. 3 shows perfect and imperfect precipitation of ammonium silicomolybdate in the mixed solutions containing 0.1 c.c. of the sodium silicate solution, 5 g. of NH_4NO_3, and the varying quantities of HNO_3 and ammonium molybdate given in the diagram. Here, the mark ○ indicates complete, and × incomplete, precipitation. Figures given below the marks show the number of c.c. of N/10 NaOH solution required for the titration of the precipitates.

Fig. 3.

That the largest and identical value described above corresponds to the correct value of silicic acid has been confirmed as follows. The mixture resulting from the titration was transferred to a casserole, evaporated to a volume of about 10 c.c., and then heated with 6–10 c.c. of concentrated sulphuric acid until white fume of the acid was vigorously given off. The residual solution was diluted with 50 c.c. of water. The insoluble silicic acid was collected, washed thoroughly, transferred to a crucible, ignited, and weighed, the weight of silica being found to correspond to the quantity of the silicate contained in the original solution.

The quantity of silicic acid present in the yellow precipitate being considered by the author to be determinable also by reducing the molybdic acid present in the same precipitate to a lower compound and by titrating the latter with an oxidizing agent, experiments have been made as follows. The final solution of the titration was evaporated in a casserole to a volume of about 10 c.c., and heated with 6–10 c.c. of concentrated sulphuric acid until white fume was given off and the liquid became blue. The residual solution was diluted with 50 c.c. of water, shaken with zinc amalgam, and titrated with N/10 $KMnO_4$ solution. The experiments have shown that this method gives accurate results more readily than that of the titration with sodium hydroxide.

A few examples of the determination of silicic acid actually made by gravimetric method and by volumetric method using both NaOH and $KMnO_4$ are given in Table 2.

Table 2.

I	II	III	IV	V	VI	VII
Quantity of the sodium silicate solution taken (c.c.)	Quantity of SiO_2 contained in the sodium silicate solution (g.)	Quantity of the N/10 NaOH solution used in the titration (c.c.)	Number obtained by dividing the number under II by the corresponding number under III	Quantity of SiO_2 determined by gravimetric method (g.)	Quantity of the N/10 $KMnO_4$ solution used in the titration (c.c.)	Number obtained by dividing the number under II by the corresponding number under VII
5	0.03106	112.60	0.000275			
3	0.01863	68.73	0.000271			
2	0.01242	45.90	0.000270			
1	0.00621	22.59	0.000274			
1	0.00621	22.54	0.000275			
2.5	0.01553	56.53	0.000274	0.01616	103.2	0.000166
0.5	0.00310	11.50	0.000270	0.00338	18.5	0.000167
0.5	0.00310	11.31	0.000274	0.00302	18.6	0.000166
			0.000273			0.000166

As shown in column IV in Table 2, the mean was found to be 0.000273. This number is justified to be a factor, by which the numbers given in column III showing the quantities of the NaOH solution in c.c. are multiplied in order to find the quantities of SiO_2; namely, c.c. of N/10 NaOH $\times$ 0.000273 = g. of SiO_2. Just in the same way the numbers in column VI are multiplied by the mean, 0.000166, in order to obtain the quantities of SiO_2; namely c.c. of N/10 $KMnO_4 \times 0.000166$ = g. of SiO_2.

The following conclusions have thus been obtained: (1) From a solution of silicate, silicic acid can be completely precipitated as ammonium silicomolybdate of yellow colour. (2) Concentration of each of nitric acid, ammonium nitrate, and ammonium molybdate suitable for complete precipitation of the yellow compound has been found experimentally. (3) The quantity of silicic acid present in the yellow precipitate can be determined either by titrating the precipitate with sodium hydroxide, or by reducing molybdic acid present in the precipitate to a lower compound and by titrating the latter with potassium permanganate. (4) Silicic acid can also be determined by gravimetric method, from the yellow precipitate or from the solution resulting from the titration with sodium hydroxide or potassium permanganate.

The author wishes to acknowledge his indebtedness to Prof. I. Wada, under whose direction this work has been carried out, and who has aided in the preparation of the manuscript for publication.

(September 10th, 1933)

QUANTITATIVE EMISSION SPECTRUM ANALYSIS OF LEAD AND CADMIUM CONTAINED IN ZINC OXIDE.

By Arata IWAMURA.

Received April 2nd, 1935. Published August 28th, 1935.

(1) **Sample Electrodes.** For the purpose of spectrographically determining very small quantities of lead and cadmium contained in zinc oxide, the oxide was first transformed into a solid conducting mass by treating merely with hydrochloric acid and then dried. A most suitable electrode was prepared in the following way:

Zinc oxide (30 g.) was gradually added to 35 c.c. of 6N HCl in a porcelain mortar and the mixture was constantly agitated, kneaded, and then moulded in a wooden mould before it was quite set, and the product was dried in an air-oven. The solid mass thus prepared was a round tablet, 3 cm. in diameter and 3 mm. thick, a round hole being made at its centre. Two such tablets containing zinc oxide with no foreign impurities except lead and cadmium were employed as the electrodes; the hydrochloric acid also contained no foreign impurities.

(2) **The Apparatus Used and the Method of Experiment.** To excite sparks between a pair of such electrodes, a transformer giving 10 kilovolts in the secondary was used. Self-inductance of a magnitude of about 62,000 cm. was always inserted in the secondary circuit. The light from an uncondensed spark between the electrodes was focused by means of a quartz lens on the slit of a small Hilger quartz spectrograph and spectrograms were thus obtained. When the sample contains a trace of lead and cadmium, the lead lines at λ4058, 3684 Å and the cadmium line at λ2288 Å were always detected on the plate. The photographic density of a line was recorded by means of Moll's recording microphotometer and for practical purposes the maximum heights of the curve for these lines measured from the neighbouring background were taken as a measure of the practical intensities of these lines.

The so-called "comparison method" was tried in analysing lead or cadmium in zinc oxide. Another method of analysing cadmium was to draw a density concentration curve in connection with the line at λ4201.8 Å and to determine graphically the content of cadmium from the density of the cadmium line in the spectrum of the sample of unknown cadmium content.

(3) **Reproducibility of the Spectrograms of Zinc Oxide Containing Lead and Cadmium and the Sensitivity of the Analysis.** Reproducibility of the spectrograms of zinc oxide electrodes containing lead was studied and it was observed that the result was reproducible within a range of $+6.5--6.1\%$. The microphotometer record proved to be sensitive within a range of $\pm 1\%$ of error. Sensitivity of the spectrographic analysis of lead or cadmium in zinc oxide was graphically determined from the density concentration relation in the following way: A series of spectrograms were taken of sparks emitted from electrodes containing varying amounts of lead or cadmium, and the practical intensities of the line were measured on microphotometer curves for various contents of lead or cadmium, and a curve connecting intensity of the line and the corresponding amount of lead or cadmium was drawn. The extrapolation of this curve gave the minimum detectable limit in the present method, i.e. the sensitivity of the method. The sensitivity of the analysis of lead in zinc oxide was thus found to be 1×10^{-6} under the conditions of the present experiment. In the case of cadmium in zinc oxide, the sensitivity was found to be 1.5×10^{-6} under the conditions of the experiment.

(4) **Influence of Acids Used for Cementing Zinc Oxide.** The influence of hydrochloric, sulphuric, and nitric acids used in cementing the zinc oxide containing 0.010% of lead or 0.050% of cadmium was determined by using the lead line at λ 4058 Å, or the cadmium line at λ 2288 A, and the densities (d_{mm}) given by the microphotometer were found as shown in Table 1.

Table 1.

Acids / d_{mm}	Hydrochloric acid	Sulphuric acid	Nitric acid
d_{mm} $\lambda = 4058$ Å	23.2	22.3	$17.5+\alpha$
d_{mm} $\lambda = 2288$ Å	15.3	9.3	9.1

It will be seen that though the densities are of the same order of magnitude, hydrochloric acid gave the most sensitive result. The sample of zinc oxide containing much carbonate was not suitable to be cemented into the electrodes for the purpose of analysing lead, because the lead lines at λ 4058 Å and 3683 Å were masked by the cyanogen bands. Such a sample containing carbonate should be heated in a porcelain dish for the purpose of decomposing carbonate and then be prepared into electrodes as described above.

(5) **Influence of Cations.** Those elements which have some spectral lines in the vicinity of the lead line at λ 4058 Å are shown in Table 2.

Table 2.

λ in Å	Origin	Intensity	λ in Å	Origin	Intensity
4077.7	Sr II	10 R	4045.8	Fe I	8 R
4066.4	Co I	7 R	4045.4	Co I	8 R
4063.6	Fe I	8 R	4044.2	K I	10 R
4056.6	Cu	2 R	4041.4	Mn I	8 R
4055.3	Ag I	8 R	4035.7	Mn I	5 R
4047.2	K I	10 R	4034.5	Mn I	8 R

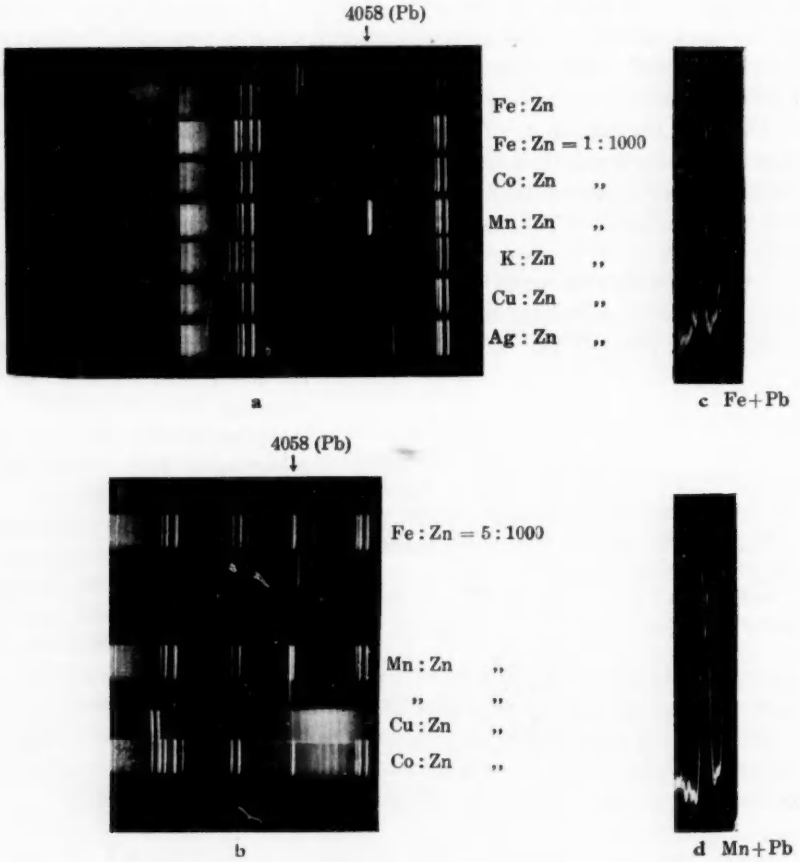


Plate I.

Now, each of the above-mentioned elements was added in small varying amounts to a definite quantity of zinc oxide sample containing a definite amount of lead till the concentration of the added element became 0.5 mol in 1000 mol of zinc oxide, and the mixture was cemented into electrodes, sparked, and spectrographed as usual. It was observed that the elements iron and manganese had marked influence upon the densities of the line at λ 4058 Å (Plate I, a and b, and the corresponding microphotometer records c and d). Hence these two elements should be avoided in preparing the electrodes for a given sample of zinc oxide. If such elements are unavoidably present, then observe the lead line at λ 3684 Å.

Now, the common elements which have some spectral lines in the vicinity of the lead line at λ 3684 Å are shown in Table 3.

Table 3.

λ in Å	Origin	Intensity	λ in Å	Origin	Intensity
3705.6	Fe I	6 R	3682.2	Fe	6
3700.3	Co	7	3679.9	Fe I	5
3687.5	Fe I	6 R	3677.6	Fe	6
3685.2	Ti II	10 R	3676.6	Co	8
3683.5	Pb	3 R	3674.2	Ni I	6
3683.1	Co	8	3669.5	Fe	6
			3669.0	Ti I	6

Iron and cobalt lines will practically coincide with the lead line at λ 3684 Å. But, it is practically very rare that cobalt occurs in zinc oxide, but iron does frequently as one of the impurities. If iron is present in zinc oxide in an appreciable quantity, then the spectrograph of higher dispersion should be employed.

With regard to the estimation of cadmium in zinc oxide, similar attention was paid. Those elements which have some spectral lines in the vicinity of the cadmium line at λ 2288 Å are shown in Table 4.

Table 4.

λ in Å	Origin	Intensity	λ in Å	Origin	Intensity
2298.2	Fe	I	2293.85 2294.30	Cu	5
2297.8	Fe	—	2292.5	Fe	—
2294.7	Cd	4	2291.1	Fe	—

Table 4. (*Concluded*)

λ in Å	Origin	Intensity	λ in Å	Origin	Intensity
2290.6	Fe	—	2286.7	Sn	3
2290.0	Ni	—	2280.2	Fe	—
2289.0	Fe	—	2279.9		
2288.1	As	3	2279.6	Ni	—
2287.6	Fe	—	2276.6	Bi	2
2287.3					

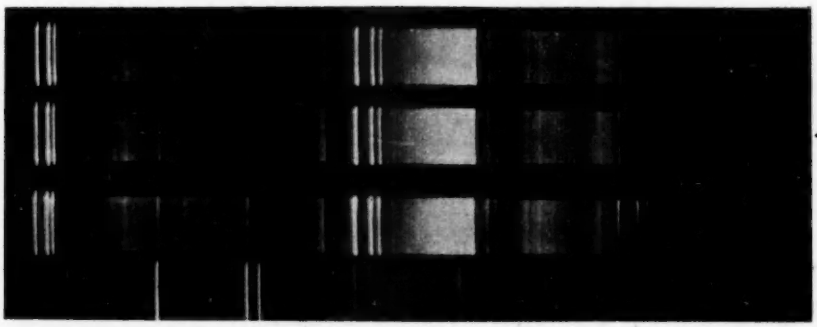
Now, each of the above-mentioned elements was added in small varying amounts, to a definite quantity of a zinc oxide sample containing a definite amount of cadmium till the concentration of the added element became 3 mol in 1000 mol of zinc oxide, and the mixture was cemented into electrodes, sparked, and spectrographed as usual. The above-mentioned elements were observed to give no detectable lines interfering with the cadmium line, λ2288 Å, and, therefore, it became evident that the addition of these elements in the concentration mentioned above would influence neither the background nor the cadmium line.

(6) **Influence of Capacity and the Self-inductance.** When condensed discharge was effected between the electrodes consisting of zinc oxide, they were easily broken and no desirable exposure could be made. The present writer was forced to use uncondensed spark discharge throughout the experiment and was unable to study the influence of capacity systematically. The introduction of capacity into the secondary circuit of the transformer was possible after the uncondensed spark discharge was continued for a few minutes, but then, there appeared air-lines which masked the lead lines in question.

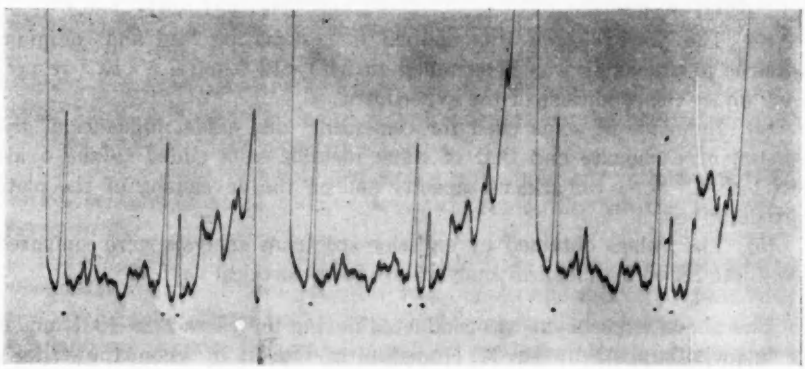
The introduction and increase of self-inductance in the secondary circuit of the transformer cleared up those air-lines and gave a clear back ground in the spectrogram. In analysing cadmium by uncondensed spark discharge nothing particular was observed.

(7) **Influence of Developers upon the Fogging of the Background of the Plate.** During the course of the experiment, the present writer has found that the hydroquinone developer which gives a strong contrast is one of the most satisfactory developers in order to make the background clear in contrast to the blackening of the lines. The use of pyrogallol developer or metol hydroquinone developer seems to be less satisfactory.

(8) **Comparison of the Results of Spectrographical Analysis of Lead or Cadmium with those of Chemical Analysis or with Theoretical Values.** Let S denote the value of lead or cadmium spectrographically obtained, C that chemically found, T the theoretical value, and Δ the divergency from the chemical or theoretical values. (See Plate II, a and b.)



a



b

Plate II.

As is shown in Table 5 the spectrographical results are generally somewhat higher than the chemical or theoretical ones, but they are of the same order of magnitude in case of lead and cadmium, the divergency being always within the limit of the permissible error.

Table 5.

	Pb %			Cd %			
	I	II	III	I	II	III	IV
S	0.0007	0.00137	0.00289	0.00137	0.01640	0.02012	0.01135
C	0.0006	0.00133	0.00270	—	—	—	—
T	—	—	—	0.00136	0.01536	0.01921	0.01082
Δ	0.0001	0.00004	0.00019	0.00001	0.00104	0.00091	0.00053
$\Delta\%$	+14+	+3−	+7−	+0.7−	+6.8−	+4.7−	4.9−

Summary.

(1) Electrodes consisting of a zinc oxide sample containing lead or cadmium, were prepared for the purpose of quantitative emission-spectrum analysis.

(2) The reproducibility of the spectrograms of the electrodes was tested, and was shown to be within -4.8 to $+6.5\%$, under the conditions of the experiment.

(3) The sensitivity of this method for estimating lead and cadmium contained in zinc oxide was determined to be 1×10^{-6} and 1.5×10^{-6} respectively under the conditions of the experiment.

(4) Influence of acids used for cementing zinc oxide, influence of the presence of carbonate and that of some metallic salts added to zinc oxide were tested. Some remarks on capacity and on the developing of the plate were described.

(5) The values obtained by emission-spectrum analysis were compared with those found by chemical analysis or with theoretical values.

The above experiment was conducted during the years 1929–1931, under the financial support by Dr. M. Momotani of Osaka, to whom the writer's most heartfelt thanks are due.

(January 5th, 1934)

Faculty of Science,
Imperial University of Kyoto.

THE ELECTROLYTIC DEPOSITION OF ZINC FROM ACID SOLUTIONS.

By Hisashi KIYOTA.

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There have been a great many works dealing with the electrolytic deposition of zinc from the various acid solutions, but none of the methods hitherto proposed can be regarded as perfect. The chief difficulty in zinc electrolysis was thought to lie in a property of zinc, which forms a spongy deposit, and an attempt was made, in this investigation, to ascertain how far this difficulty might be overcome and to establish a convenient method for the quantitative analysis of zinc.

Throughout all the experiments, a platinum basin of about 150 c.c. capacity previously plated with copper was employed as the cathode, and a platinum disk which could be rotated as the anode.

In order to find out what results were attainable when the methods previously known were followed with this apparatus, a series of experiments was performed according to the methods given by F. Spitzer,[1] A. Fischer and R. J. Boddaert,[2] F. F. Exner,[3] and L. H. Ingham.[4] None of these methods, however, gave satisfactory results, all producing the deposit in spongy form, and some giving a deposit adhering to the cathode so loosely that even washing could not be effected.

The best results were obtained by the present author with an acetic acid solution containing some sodium acetate. An outline of the experiment follows.

The sample of zinc was taken below 0.5 g. from the analytical standpoint. The suitable volume of the electrolyte was found to be about 125 c.c. To see the effects of many important factors they were fixed in a range suitable for the analytical purpose and the electrolysis was carried out, changing at a time one factor only to be tested. The following results were obtained: (A) Zinc tended to deposit in a fine crystalline form with a metallic lustre giving a negative error in the cases where (1) the concentration of the acetic acid

(1) F. Spitzer, *Z. Elektrochem.*, **11** (1905), 404.

(2) A. Fischer and R. J. Boddaert, *Z. Elektrochem.*, **10** (1904), 946.

(3) F. F. Exner, *J. Am. Chem. Soc.*, **25** (1903), 899; *Chem. Zentr.*, **74** (1903), (2), 1210.

(4) L. H. Ingham, *J. Am. Chem. Soc.*, **26** (1904), 1270; *Chem. Zentr.*, **75** (1904), (2), 1758.

was comparatively great, (2) the quantity of the sodium acetate was comparatively small, (3) the current density was comparatively small, (4) the temperature of the electrolyte was comparatively high, and (5) the rotation of the anode was comparatively quick. (B) In the cases reverse to the above, zinc tended to deposit in a spongy form giving a positive error.

The author investigated further by adjusting the factors and found out a method for the electrolytic determination of zinc. This method is very convenient and give very accurate results. It is carried out as shown below.

(1) The sample was used in the form of zinc sulphate, 6 g. of crystalline sodium acetate and various amounts of acetic acid being added. Water was added up to 125 c.c., and the solution was electrolyzed. (2) The concentration of the acetic acid was adjusted according to the amount of zinc present: for 0.5 g. of zinc, 0.15–0.21 normal; for 0.3 g., 0.21–0.27 normal; and for 0.1 g., 0.27–0.33 normal. (3) The electrolysis was begun at room temperature. The regulation of the temperature of the electrolyte was unnecessary. (4) The anode was rotated at the rate of 1500–1700 turns per minute. (5) The current density was maintained at 0.5–0.6 amp./dm^2, till the potassium ferrocyanide reagent ceased to give the reaction of zinc—the main electrolysis—and it was then raised to 3–4 amp. and continued for about 10 minutes. (6) The duration of the main electrolysis varied from about 35 minutes to about 80 minutes according to the amounts of zinc: for 0.5 g. zinc, 65–80 min.; for 0.3 g., 50–60 min.; for 0.1 g., 35–40 min.; and for 0.001 g., 0 min. (7) At the end of the electrolysis, the cathode was washed with water without stopping the current and the rotation of the anode, then washed with alcohol, and ether, dried, and weighed. (8) In these experiments, the errors were always within 0.1 mg.

The influences of such substances as sodium sulphate, ammonium sulphate, ammonium acetate, sodium chloride, and sodium nitrate on the zinc deposition was investigated. The presence of sodium sulphate, ammonium sulphate, and ammonium acetate had no significantly harmful influence, when their concentration was lower than 0.15 normal. The nitrate greatly retarded the deposition of zinc and tended to deposit the metal in a spongy form. The effect of the chloride was not nearly so bad as that of the nitrate, and still it was often a cause of negative error.

The author wishes to express his sincere thanks to Prof. Motooki Matsui, under whose guidance and encouragement this work was carried out.

Kyoto Women's College,
Katsura, Kyoto.

ON THE ELECTROLYTIC DEPOSITION OF METALS FROM THEIR PYROPHOSPHATE SOLUTIONS.

By Shiro KOYANAGI.

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Pyrophosphates of various metals dissolve in alkali pyrophosphate solutions to form complex salts which are generally thought to have such compositions as represented by $Na_2[M^{II}P_2O_7]\cdot xH_2O$ or $Na[M^{III}P_2O_7]\cdot xH_2O$. As to the electrolytic deposition of metals from these complex pyrophosphate solutions A. Brand[1] conducted some experiments long ago. The present author has studied the electrolytic deposition of nickel, cobalt, copper, zinc, and cadmium from their complex pyrophosphate solutions with Classen's electrode in order to find best conditions for the analysis of these metals. Iron was found not to be deposited completely from the pyrophosphate solution. For the other metals, especially for zinc and cadminum which were hitherto known to give no satisfactory deposit, the method was found to give very trustworthy result.

Nickel. Nickel sulphate was taken as the sample, and its pyrophosphate solution mixed with some ammonium carbonate was used as the electrolyte.

Ni (as $NiSO_4\cdot 7H_2O$)	$Na_4P_2O_7\cdot 10H_2O$	$(NH_4)_2CO_3$	Volume	Amp.	Volt	Temp.	No. of rotation	Time
0.1–0.3 g.	3.0–5.0 g.	3.0–4.0 g.	120 c.c.	1.0–2.0	6.0–7.0	ord. temp.	800 per min.	90–120 min.

Cobalt. Cobalt sulphate was used for analysis. The amount of cobalt taken for analysis should be kept below 0.2 g.; otherwise the deposit acquires somewhat dark appearance.

Co (as $CoSO_4\cdot 7H_2O$)	$Na_4P_2O_7\cdot 10H_2O$	$(NH_4)_2CO_3$	Volume	Amp.	Volt	Temp.	No. of rotation	Time
0.1–0.2 g.	4.0–5.0 g.	1.0–2.0 g.	125 c.c.	1.0–1.5	6.0–7.0	ord. temp.	800 per min.	70–100 min.

Copper. The pyrophosphate solution mixed with some ammonium nitrate was found to give the best result.

(1) *Z. anal. Chem.*, **28** (1889), 581.

Cu (as $CuSO_4 \cdot 5H_2O$)	$Na_4P_2O_7 \cdot 10H_2O$	NH_4NO_3	Volume	Amp.	Volt	Temp.	No. of rotation	Time
0.1–0.3 g.	7.0–8.0 g.	3.0–5.0 g.	120 c.c.	1.0–1.5	4.0–5.0	ord. temp.	800 per min.	90–120 min.

Zinc. Zinc pyrophosphate solution with the addition of ammonium nitrate was taken as the electrolyte, and electrolysis was conducted with the cathode previously electroplated with copper.

Zn (as $ZnSO_4 \cdot 7H_2O$)	$Na_4P_2O_7 \cdot 10H_2O$	NH_4NO_3	Volume	Amp.	Volt	Temp.	No. of rotation	Time
0.2 g.	7.0 g.	0.5–1.0 g.	125 c.c.	1.0–1.5	6.0–7.0	ord. temp.	500 per min.	120 min.

Cadmium. The conditions for its analysis were very similar to those for zinc determination.

Cd (as $3CdSO_4 \cdot 8H_2O$)	$Na_4P_2O_7 \cdot 10H_2O$	NH_4NO_3	Volume	Amp.	Volt	Temp.	No. of rotation	Time
0.1–0.2 g.	9.0 g.	1.0 g.	125 c.c.	2.0–2.5	5.5–6.0	ord. temp.	500–600 per min.	120 min.

In conclusion the author wishes to express his thanks to Prof. M. Matsui for his kind advices.

(April 15th, 1934)

PRECIPITATION OF ALUMINIUM WITH HYDROGEN AMMONIUM CARBONATE.[1]

By Toshio KOZU.

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In the previous communication[2] it was reported that aluminium is precipitated with a hydrazine solution saturated with carbon dioxide. If, by a similar treatment, ammonia might be made equally suitable for aluminium analysis it would be a very useful precipitant of aluminium, perhaps surpas-

(1) An abstract from the original, *Mem. Coll. Sci., Kyoto Imp. Univ.*, A, 1934, 17

(2) *J. Chem. Soc. Japan*, **54** (1933), 682.

sing all others. It was for the hope of accomplishing this purpose that the present work was undertaken.

The *p*H value of a solution of commercial ammonium carbonate having the concentration of about one molar, is 8.70 at 21°. When this solution is cooled with ice and saturated with carbon dioxide, hydrogen ammonium carbonate begins to crystallize out on the bottom of the vessel, the *p*H value of the solution at this instant being lowered to 7.6. The molar solution of hydrogen ammonium carbonate thus separated was found to have *p*H 7.5 at 20°, which changed to 7.8 after three weeks. To prepare a reagent suitable for aluminium analysis, it is not necessary to isolate hydrogen ammonium carbonate in solid form; we have only to saturate a molar solution of commercial ammonium carbonate with carbon dioxide till hydrogen ammonium carbonate begins to separate out, and then to expel the excess of carbon dioxide dissolved in it by exposing the solution to a reduced pressure of about 15 mm.

Gravimetric Analysis. To determine aluminium gravimetrically, a potassium alum solution containing 0.1446 g. Al_2O_3 in about 30 c.c. with two drops of bromo-thymol blue was slowly treated with hydrogen ammonium carbonate under constant agitation, till the indicator exhibited blue colour. The precipitation of aluminium was always accompanied by the evolution of carbon dioxide. After standing for 20 minutes the vessel containing the precipitate was warmed on a water bath for 40–60 minutes with occasional shaking. The heating should be continued till ammonia gas, recognizable by its odour, ceases to evolve. The *p*H value of the mother liquor at this instant was observed to be 7.45 at 21°. The precipitate was then filtered and washed with water warmed to 50–60°, till the filtrate no longer showed the reaction of SO_4''. It was first dried at 100°and then ignited at 1100°. The results of analysis are shown in Table 1. Even a trace of aluminium was never found in the filtrate.

Table 1. Al_2O_3(taken): 0.1446 g.

Al_2O_3 found (g.)	Error (g.)	Al_2O_3 found (g.)	Error (g.)
0.1445	−0.0001	0.1446	−0.0000
0.1448	+0.0002	0.1442	−0.0004
0.1442	−0.0004	0.1444	−0.0002
0.1443	−0.0003	0.1451	+0.0005
0.1447	+0.0001	0.1444	−0.0002

To determine the composition of the aluminium compound precipitated by hydrogen ammonium carbonate the precipitate formed at room tempera-

ture was left to stand for a night, filtered with a glass filter, and well washed with water. After water was removed by suction as completely as possible, the precipitate was placed over calcium chloride in a vacuum desiccator. The precipitate, which had a powdery amorphous form, gave the following results on analysis: Al_2O_3, 47.71; H_2O, 35.01; CO_2, 17.28. Calc. for $4Al(OH)CO_3 \cdot 6Al(OH)_3 \cdot 9H_2O$: Al_2O_3, 48.72; H_2O, 34.44; CO_2, 16.82%.

The formulas hitherto given by several authors for basic aluminium carbonate differ from one another and also from that of the present author, perhaps owing to divergence in the conditions under which the precipitate was prepared.

The solubility of the basic aluminium carbonate in water was found to be 0.00242 at 20.5°, and 0.00307 at 21.5° per 1000 c.c.

When precipitated from a very dilute solution, basic aluminium carbonate takes the form of very fine particles which when warmed with mother liquor, become unsuitable for analytical treatment, being changed thereby into a colloidal form.

The most suitable concentration was found to be 47.4–23.7 millimol solution of potassium alum, that is, the solution containing 1.3459 g. of potassium alum in 30–70 c.c.

Procedure. The procedure of the new method for analysing aluminium as its oxide may be stated as follows: To a solution containing 0.05–0.1 g of aluminium in the form of potassium alum in 30 c.c.–40 c.c. about one molar hydrogen ammonium carbonate solution is slowly added with stirring, till bromo-thymol blue, added beforehand, turns blue. As the evolution of carbon dioxide ceases at this stage the end point of the reaction is easily recognized without the use of an indicator. After standing for 20–30 minutes the precipitate is warmed on a water bath, whereupon carbon dioxide accompanied by some ammonia is again evolved. Heating is continued for 40–60 minutes till the odour of ammonia becomes unrecognizable. Add some water, if necessary, taking care to keep the total volume of the mother liquor always less than 50 c.c. The precipitate is then filtered and washed with warm water of about 60° till the filtrate shows no reaction of SO_4''. After drying at about 100° the precipitate together with the filter paper is placed in a crucible and ignited at about 1100°. When the crucible is weighed, it must be enclosed tightly in a well-stoppered weighing tube.

Summary.

(1) Hydrogen ammonium carbonate prepared by saturating the solution of commercial ammonium carbonate with carbon dioxide may conveniently be used for quantitative precipitation of aluminium.

(2) The precipitate formed with hydrogen ammonium carbonate at ordinary temperature is fairly stable in a solution having the *p*H value of 7.6, and its composition is represented by $4Al(OH)CO_3 \cdot 6Al(OH)_3 \cdot 9H_2O$.

(3) The solubility of the basic carbonate in water is found to be 0.00242 g. per 1000 c.c. at 20–21°.

(4) The analytical procedure for gravimetric determination of aluminium with hydrogen ammonium carbonate is given.

(5) Several precautions which are to be taken in the analytical treatment of basic aluminium carbonate are fully described.

In conclusion the author wishes to express his warm thanks to Prof. Motooki Matsui for his kind guidance and valuable suggestions.

(June 10th, 1934)

ON THE ANALYSIS OF BISMUTH BY MEANS OF SELENIOUS ACID.

By Otozo FUNAKOSHI.

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Berg and Teitelbaum[1] measured the sensitivity of formation of bismuth selenite precipitate in 1/3 and 1/4 normal nitric acid, and they fixed the limit of detectability of bismuth at 0.000016 g. in 5 ml., i.e. 1:300000. They state that an accurate gravimetric analysis can be made by making the precipitate, having the composition $Bi_2(SeO_3)_3 \cdot H_2O$, anhydrous by boiling in the mother liquor and then by properly drying and weighing.

For satisfactorily accomplishing the analysis of bismuth by the use of selenious acid as the precipitant, it is important to have a clear knowledge of the relation of the acid concentration to the formation of the precipitate, and of the behaviour of other metals upon selenious acid. The present investigation was started for clarifying these points.

The Material and Reagents. The material for the experiments was prepared from the selenium of the Hitachi Mine by heating it in the stream of oxygen, purifying the selenium oxide by repeated resublimation, adding a

(1) *Z. anorg. allgem. Chem.*, **189** (1930), 101.

small quantity of freshly boiled water, and evaporating on the water-bath. For oxidizing any liberated selenium, the evaporation was continued with the addition of 3–4 ml. of concentrated nitric acid, and the residue was finally heated over direct flame until white fumes were developed. The selenious acid thus prepared was used as a 5 per cent. aqueous solution.

Kahlbaum's bismuth nitrate of the superior quality and Merck's nitric acid of sp. gr. 1.4 for analytical use were employed for making 1% solution of the former and 0.5 N solution of the latter.

The Sharpness of the Reaction leading to the Formation of Bismuth Selenite Precipitate. For the purpose of ascertaining the limits of formation of bismuth selenite precipitate, observations were made under the conditions of reaction detailed in Table 1.

Table 1.

Bi taken (g)	Selenious acid solution (ml.)	Total volume (ml.)	Nitric acid normality	Limit of formation of ppt.	Remarks
0.000043	1.3	4.3	1/3.3	1×10^{-5}	Immediate white turbidity; crystalline particles on heating. Clear supernatant liquid.
,,	1.6	8.6	1/4.3	2×10^{-5}	Fine cryst. particles on heating 1 minute.
,,	1.9	12.9	1/3.9	3×10^{-5}	Fine cryst. particles on heating 2 minutes.
,,	2.05	15.05	1/3.8	3.5×10^{-5}	Fine cryst. particles on heating 2 minutes.
,,	2.0	17.2	1/3.7	4.0×10^{-5}	A few fine cryst. particles on heating 2 minutes.
,,	2.5	21.5	1/3.6	5.0×10^{-5}	A few fine cryst. particles on heating 2-3 minutes. Clearly distinct from the blank test.
0.000086	1.5	4.5	1/3.4	5.0×10^{-5}	The same as above.

From the above-given results, it is seen that 0.00001 g. of Bi in 5 ml. can be detected when the final acid normality is 1/4. The sensitiveness is 1:500000.

The Influence of Acid Strength on the Sensitivity of Precipitation. If the acidity is above 0.86 N in nitric acid, the precipitation of bismuth selenite is incomplete even when 0.00086 g. of Bi is contained in 6 ml. of the solution. Beyond 1 N in acidity, there is no precipitation at all. It is found that, for the complete precipitation, the acidity must be below 0.5 N. The influence of hydrochloric acid is about the same as that of nitric acid. Sulphuric acid is, however, very much weaker in this respect, for up to 1.4 N it does not hinder the precipitation of a solution of 0.00086 g. Bi in 5–6 ml., while nitric acid completely prevents the precipitation already at 0.9 N. When heated, nitric acid prevents the precipitation at 0.6 N while with sulphuric acid the limit is reached only at 0.9 N.

The Action of Selenious Acid upon the Salts of other Metals. Such metals as Cu, Cd, $Fe^{\cdot\cdot}$, Al, Ni, Co, Mn, Zn, Ca, Li, Na, and K are not precipitated by selenious acid and can be separated from bismuth by its use. Iron and chromium in the trivalent state are precipitated within 15 minutes by heating at the concentration of 4.5×10^{-5} and 5×10^{-4} respectively. The iron precipitate is dissolved by 1/6 N HNO_2, 2/7 N HCl, and 1/3 N H_2SO_4. The chromium precipitate is dissolved by 1.7 N HNO_3, 0.7 N HCl, and 1.2 N H_2SO_4.

Solution of such metals as Hg, Pb, $Sn^{\cdot\cdot}$, Sb, and Ag are precipitated by selenious acid at the concentration of 7.5×10^{-4} to 1.5×10^{-5}. The lead precipitate is readily soluble in HNO_3 or HCl. Solutions of Ba, Sr, Mg, Ti, and Th are precipitated at the concentration of 5×10^{-4} to 2×10^{-5}, and the precipitates of Ba, Sr, and Th are dissolved in the presence of 1.1–2 N HCl, or 0.7–1.2 N HNO_3. Among the twelve elements mentioned above which are precipitable with selenious acid, silver, ferric iron, barium, titanium, and thorium are more sensitive than the rest, and consequently their presence makes the qualitative detection of bismuth somewhat uncertain. As bismuth, mercury, and lead have the common properties of being precipitated by H_2S and of not dissolving in ammonium sulphides, their detection will have nothing to gain by the use of selenious acid reagent.

The Quantitative Determination of Bismuth with Selenious Acid. Fifty ml. of 1% solution of bismuth nitrate are diluted to 80–90 ml. and nitric acid is added to the resultant strength of 0.35–0.38 N. The solution is heated to boiling and the selenious acid reagent is added slowly with stirring. After the completion of precipitation, an excess of a few ml. of the reagent is added while still keeping the solution boiling for some time. After cooling the precipitate is filtered and washed with cold water until there is no selenious acid remaining in the filtrate. The precipitate is well dried in the air and is then ignited rather strongly from the outset over the Bunsen burner for an hour (If the heating is begun slowly with a small flame, there is

a danger of a loss of bismuth in the stream of subliming SeO_2 formed by the decomposition of the precipitate). After cooling it is weighed in the usual manner.

It is to be noted here that if the heating is done, as suggested by Berg and Teitelbaum, at first for an hour at 50° and for another hour at 105°–115°, and the precipitate is weighed as $Bi_2(SeO_3)_3$, it is rather difficult to attain a constant result (Table 2).

Table 2.

Product finally weighed	Theoretical value (g.)	Values found (g.)		
		1	2	3
$Bi_2(SeO_3)_3$	0.4031	0.3948	0.4029	0.3979
Bi_2O_3	0.2349	0.2348	0.2349	0.2347

It is seen from the Table that a more accurate and constant result is obtained by strongly igniting the bismuth selenite precipitate and weighing the product as Bi_2O_3, than by drying is at 105°–115° and weighing as $Bi_2(SeO_3)_3$.

The author wishes to express his deep gratitude to Professor Matsui for his valuable guidance.

(August 5th, 1934)

A NEW GRAVIMETRIC METHOD FOR THE DETERMINATION OF LEAD AS LEAD SALICYLALDOXIME AND ITS SOLUBILITY MEASUREMENT BY USING Th B AS RADIOACTIVE INDICATOR.

By Masayoshi ISHIBASHI and Haruo KISHI.

Received May 10th, 1935. Published August 28th, 1935.

I. Gravimetric Determination of Lead as Salicylaldoxime Compound. An excellent method of quantitatively determining copper as a salicylaldoxime compound has been proposed by F. Ephraim.[1] The present authors

(1) F. Ephraim, *Ber*, **63** (1930), 1928.

have now found a new gravimetric method for the analysis of lead using salicylaldoxime.

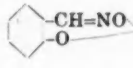
Material Used. The sample used was Kahlbaum's lead acetate for analysis, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, the composition of which was proved to be quite exact by the gravimetric determination of lead as the chromate. Of this substance, 7.3228 g. was dissolved in 1 liter; and this solution contains 0.0400 g. of lead in 10 ml.

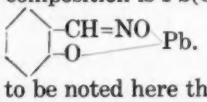
Salicylaldoxime was prepared from salicylaldehyde and hydroxylamine hydrochloride and purified by repeated recrystallization from ligroin. The colourless crystals thus obtained had the melting point 63°C. The substance had some tendency to get somewhat coloured when stored. One gram of it is dissolved at room temperature in 5 ml. of alcohol and the solution is slowly poured into 95 ml. of pure water warmed to about 80°C. A little of the oxime which may remain at first as a turbid suspension is gradually dissolved away. The solution is now filtered after a thorough stirring and the 1% solution of the oxime thus prepared is used for precipitating the lead salt.

Procedure. Twenty-five ml. of the lead acetate solution is diluted with pure water to about 50 ml. and treated with a slight excess of salicylaldoxime. Ten per cent. ammonia water is then slowly added so as to make the *p*H of the solution greater than 6.5. For this purpose, neutral red (*p*H = 6.8—8.0) or phenolphthalein (*p*H = 8.2—10.0) is used as a convenient indicator. After clarifying the turbid mother liquor by stirring, it is allowed to stand about an hour. The easily filtrable precipitate of slightly yellow colour is transferred to a glass filter, washed with 20% alcohol, and filtered by suction. It is thoroughly dried at about 105°C., cooled, and weighed as usual. The result is shown in Table 1.

Table 1.

No.	Salicylaldoxime added (g.)	Pb-Salicylaldoxime found (g.)	Pb		Difference (g.)
			added (g.)	found (g.)	
1	0.08	0.1648	0.1000	0.1000	0.0000
2	0.08	0.1647	0.1000	0.0997	−0.0003
3	0.08	0.1646	0.1000	0.0996	−0.0004
4	0.08	0.1647	0.1000	0.0997	−0.0003
5	0.08	0.1645	0.1000	0.0996	−0.0004

Pb :  Pb = 0.6054.

For deciding upon the composition of lead salicyladoxime, the quantitative determination of lead and nitrogen in it was made. Lead in a weighed quantity of the substance dried at 105°C. was precipitated in acetic acid solution as lead chromate and weighed. Nitrogen was determined as ammonia by the Kjeldahl method. As shown in Table 2 the results prove that the probable composition is $Pb(C_7H_5O_2N)$ and suggest that the allowable constitution is  Pb.

It is to be noted here that, in copper salicylaldoxime, one atom of copper is combined with two molecules of salicylaldoxime, while, in lead salicylaldoxime, one atom of lead is combined with only one molecule of the aldoxime. Similar examples are found among other oxime compounds of metals, which we intend to report in another connection.

Table 2.

Pb-Salicylaldoxime taken (g.)	$PbCrO_4$ found (g.)	Pb			Difference %
		g.	%	as $Pb(C_7H_5O_2N)$ %	
0.1640	0.1558	0.09988	60.81	60.54	+0.27
Pb-Salicylaldoxime taken (g.)	NH_3 found (g.)	N			Difference %
		g.	%	as $Pb(C_7H_5O_2N)$ %	
0.1642	0.007627	0.006272	3.82	4.09	−0.27

The hydrogen ion concentration of the precipitating solution, from which lead salicylaldoxime was completely precipitated, was determined with indicators in the following way. A strong acetic acid solution of lead acetate was first prepared, in which the addition of an excess of the salicylaldoxime solution formed no precipitate. This acid mixture was divided into several portions, to each of which a separate indicator was added and ammonia water was poured drop by drop so as to produce a definite colour grade showing a definite *p*H value. The reaction mixtures were allowed to stand for an hour, and then filtered. Each of the filtrates was now tested for lead with sodium sulphide solution to ascertain the degree of completeness of precipitation. Indicators used for this purpose were tropeolin 00 ($pH = 1.3-3.0$), methyl orange ($pH = 3.1-4.4$), methyl red ($pH = 4.2-6.3$), neutral red ($pH = 6.8-8.0$), and phenolphthalein ($pH = 8.2-10.0$). It was found that, at $pH \leqq 6.5$, the filtrate formed no precipitation of lead sulphide showing that the pre-

ceding precipitation of lead salicylaldoxime was complete. By utilizing the differences of *p*H values produced in this way, the authors[2] succeeded in separating and determining copper and lead in a mixture.

II. Solubility Determination of Lead Salicylaldoxime by Using Th B as the Radioactive Indicator. There are four methods used ordinarily in determining solubilities of difficultly soluble compounds; namely, (1) a definite quantity of the saturated solution is evaporated to dryness and the dry residue weighed; (2) the electrical conductivity of the saturated solution is determined and the solubility calculated; (3) the single potential between the electrode and ions of the dissolved salt is measured and the solubility calculated; (4) the solubility product is first found from the equilibrium constant and the solubility calculated.

Each of these methods is accompanied by a theoretical limitation and consequently the result gives only a conditional value. The fifth method described below is free from this defect. (5) G. v. Hevesy and F. Paneth[3] first used in the determination of the solubility of lead chromate Ra D as indicator. Generally, when a radioactive isotope of the metal, whose salt is to be measured, is used as an indicator, the solubility found represents the total quantity of the dissolved part no matter whether that part is ionized or hydrolyzed or not. Moreover, the manipulation of this method is not complex at all and the result is believed to be far more rational than that obtained with the four ordinary methods.

The solubilities of some of difficultly soluble organo-metallic complex salts are known, but, as they were determined by the first method cited above, there is no safeguard as to their exactness. The present authors have succeeded in obtaining exact solubility of lead salicylaldoxime in water with the use of Th B ($T = 10.6$ h.), the radioactive isotope of lead.

Radio-thorium was taken as the mother substance of Th B. In the upper part of the receptacle for radio-thorium, a small plate of platinum, which is easily inserted or removed, is suspended. Between the receptacle (+) and the platinum plate (−) a pure water resistance is inserted and a potential of 200 volts is applied with both the terminals connected with the earth. As soon as thorium-emanation is evolved from radio-thorium through the step of Th X, it is caught on the platinum plate and Th A, Th B, Th C, etc. are caused to deposit on it. On taking off the platinum plate, Th A ($T = 0.14$ sec.) is rapidly disintegrated and leaves Th B, Th C, etc. behind. It is to be

(2) M. Ishibashi and H. Kishi, *J. Chem. Soc. Japan*, **55** (1934), 1067.
(3) G. v. Hevesy and F. Paneth, *Z. anorg. allgem. Chem.*, **82** (1913), 223.

noted here that the radio-activity (β-ray) of Th B is too weak and insufficient, so that what we measure practically is the intensity of α- and β-rays evolved from Th C produced from Th B. For this reason, it is necessary that Th B and Th C are in transient equilibrium ; if the radio-activity of radio-thorium is strong and the duration of exposure of the platinum plate short, an allowance of a certain period of time will be necessary before the attainment of this transient equilibrium. In our case, however, the quantity of radio-thorium was small and the radio-activity weak, so that about one week's exposure of the platinum plate was necessary for performing one experiment. In such a case, it is to be easily presumed, and is also proved, that the transient equilibrium is practically attained at the moment of the removal of the platinum plate.

The measuring apparatuses used were the radioscope of the Rikagaku-kenkyujo, an accurate watch, and a stop-watch. According to the theoretical formula expressing the decline of radioactivity, $I_t = I_0 e^{-\lambda t}$, the value for a definite instant was calculated from the experimental values at various instants. I_0 is the radioactivity at the start, I_t that at the end of a period t, λ the disintegration coefficient, which is 0.0654 (h.$^{-1}$) for Th B.

Procedure. The platinum plate suspended above radio-thorium for about one week was treated with about 5 ml. of hot concentrated acetic acid to dissolve the deposited Th B, Th C, etc. The solution was diluted to about 50 ml. with pure water and exactly one ml. of it was taken from a burette on a watch glass. It was now evaporated up on the water bath and dried in the air bath at about 120°C. The radioactivity was measured with the residue after its complete cooling (Table 3). Radioactivity measurements made later on were calculated back to that of this first instant.

On the other hand, 20 ml. of the same radioactive indicator solution were measured off from the burette and poured into a beaker of 100 ml. capacity ; a weighed quantity of lead acetate was added to it and dissolved by stirring with a glass rod so as to distribute the acetates of Th B and Th C homogeneously in the lead acetate solution. The salicylaldoxime solution was now added in excess. After adding phenolphthalein, ammonia water was slowly added with constant agitation until pink colour was produced. After allowing to stand for about an hour, the precipitate was collected and washed in the usual way.

The wet lead salicylaldoxime thus prepared was placed in an Erlenmeyer flask of about 200 ml. capacity, about 100 ml. of pure water was added to it, and the flask was tightly closed with a rubber stopper and introduced to a thermostat at 25°C. It was kept in rotation for 24 hours for the purpose of the complete saturation. Finally it was taken out from the thermostat and

filtered. About 20 ml. of the first filtrate were thrown away for avoiding the concentration change caused by the adsorption on filter paper. Out of the remaining 80 ml. of the filtrate, 50 ml. are accurately measured out into the evaporating dish, evaporated on the water bath, and dried in the air bath as before. After cooling, the radioactivity was measured (Table 4 and Table 5).

Table 3.

Natural discharge			Radioactivity for 1 ml.			
Measuring time elapsed (min.)	Reading of scale divisions	Number of scale divisions per min.	Measuring time elapsed (min.)	Reading of scale divisions	Number of scale divisions per min.	Corrected value (I_0)
0.00 20.00	60.0 50.0	0.50	0.00 0.77	60.0 40.0	26.0	26.0–0.5 = 25.5

Table 4.

Radioactivity for 20 ml.	$Pb(C_7H_5O_2N)$ equivalent to 0.0318 g. of $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ (g.)	$Pb(C_7H_5O_2N)$ corresponding to radioactivity of one scale division per min. (g.)
Number of scale divisions per min. $25.5 \times 20 = 510$	$\frac{0.0318 \times 0.5463}{0.6054} = 0.0287$ $Pb/Pb(C_2H_3O_2)_2 \cdot 3H_2O = 0.5463$ $Pb/Pb(C_7H_5O_2N) = 0.6054$	$0.0287/510 = 0.0000564$

Table 5.

Natural discharge			Radioactivity for 50 ml.				
Measuring time elapsed (min.)	Reading of scale divisions	Number of scale divisions per min.	Measuring time elapsed (min.)	Reading of scale divisions	Number of scale divisions per min.	Corrected value	
						I_t	I_0
0.00 24.39	50.0 40.0	0.41	0.00 17.86	50.0 40.0	0.56	0.56–0.41 = 0.15	1.14 (t = 31 hs.)

It is seen from Table 5 that the radioactivity of the dried material from 50 ml. of the saturated solution of lead salicylaldoxime is 1.14, and hence the radioactivity for one liter of it is $1.14 \times 20 = 22.8$. From Table 4 it is known that the weight of lead salicylaldoxime corresponding to unit radioactivity is 0.0000564 g. and hence the solubility in 1 liter of pure water at 25°C. must be $22.8 \times 0.0000564 = 0.0001287$ g. $\fallingdotseq 1.29 \times 10^{-3}$ g.

In the same way, the result of the second experiment with the saturation time of 15 hours was found to be 1.61×10^{-3} g., and that of the third experiment with the saturation time of 27 hours was found to be 1.22×10^{-3}g. The minimum time necessary for the complete saturation is thus found to be somewhere within 15 hours of rotatory agitation.

Table 6. Solubility per liter at 25°C.

Pb-Salicylaldoxime		Pb
(g.)	(mol)	(g.)
1.29×10^{-3} 1.61×10^{-3} } mean 1.37×10^{-3} 1.22×10^{-3}	3.8×10^{-6} 4.7×10^{-6} } mean 4.0×10^{-6} 3.6×10^{-6}	7.79×10^{-4} 9.75×10^{-4} } mean 8.31×10^{-4} 7.39×10^{-4}

Summary.

(1) Lead is quantitatively precipitated as salicylaldoxime compound from a neutral and a strongly ammoniacal solution of $p\mathrm{H} \gtrless 6.5$.

(2) The composition of the material precipitated and dried at about 105°C. is possibly $Pb(C_7H_5O_2N)$.

(3) The solubility of lead salicylaldoxime in pure water at 25°C., measured by the use of radioactive isotope Th B as indicator, is 1.37×10^{-3} g. per liter, i.e., 4.0×10^{-6} mol/l.

The authors wish to express their gratitude to Professor G. v. Hevesy of the University of Freiburg i.B., Germany, for his generosity to send them the sample of radio-thorium used in this experiment.

THE WATER IN INORGANIC COMPOUNDS. II. THE WATER CONTENT OF ODO ACID CLAY AT VARIOUS TEMPERATURES IN AIR CURRENT OF THE CONSTANT WATER VAPOUR PRESSURE.

By Minoru NAKAMOTO.

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Studies on the water in Odo acid clay have been reported by many investigators.[1] The present writer,[2] too, has often done similar researches, one of which will be briefly described below.

The whole apparatus used in our experiment is shown in Fig. 1. The air current was produced and purified in A, B, C, and D, and, after saturated with the water vapour in the thermostat (Fig. 2), was introduced into the reaction furnace in which the platinum crucible containing the sample was hung as shown in Fig. 1. The weight change of the sample was observed by Honda's thermobalance.[3] The temperatures of the thermostat (T_2), connec-

Table 1.

g (g.)	P mm. Hg	T	P'mm. Hg	p mm. Hg	V (c.c.)	$\frac{V}{\text{Time}}$ c.c./min.	π mm. Hg
0.1151	761.5	291.9	771.0	16.0	2000	3.0	54.5
0.1787	763.0	292.6	773.0	17.0	3000	2.1	56.4
0.1806	759.0	292.6	769.0	17.0	3000	2.3	57.0
0.1198	764.0	291.1	772.0	15.5	2000	2.0	56.5
0.1139	763.5	292.1	773.5	16.5	2000	5.3	54.0
0.1173	762.5	292.1	772.5	16.5	2000	16.7	55.5
0.1170	755.0	292.1	764.5	16.5	2000	13.6	55.4
0.1783	765.0	290.1	773.0	14.5	3000	12.9	55.7
0.1183	756.5	289.1	764.5	13.6	2000	14.1	55.3
0.1782	763.0	291.1	771.0	15.5	3000	13.4	56.1
0.1775	758.5	291.6	768.0	16.0	3000	23.4	55.9
0.1782	763.0	290.6	771.0	15.0	3000	23.4	55.9

(1) *J. Soc. Chem. Ind., Japan*, **32** (1929), 997; *ibid.*, **33** (1930), 69, 304, 1040; *ibid.*, **34** (1931), 680; *J. Chem. Soc. Japan*, **51** (1930), 673, 755.
(2) *J. Chem. Soc. Japan*, **50** (1929), 473; *ibid*, **54** (1933), 717, 772.
(3) *Kinzoku-no-Kenkyu*, **1** (1924), 542.

tion tube E (T_3), and the furnace (T_4) were strictly conditioned as follows: $T_2 < T_3 < T_4$. To confirm the saturation of the air current with the water vapour, the vapour pressure was calculated by the following formula from the experimental data in Table 1, which were determined at the temperatures: $T_2 = 40°C.$, $T_3 = 55°C.$, $T_4 = 65°C.$: $\pi = \dfrac{62370\,gPT}{(P'-p)MV+62370\,gT}$, where π

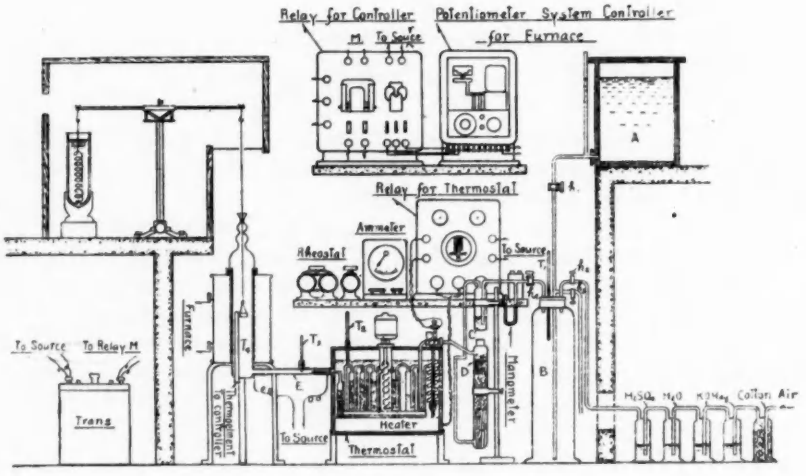

Fig. 1.

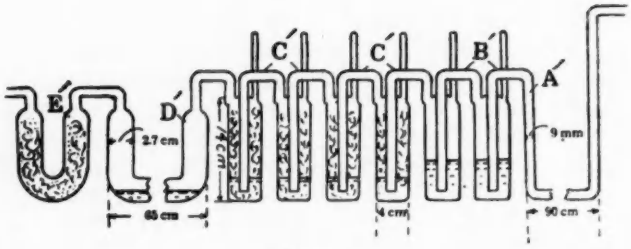

Fig. 2.

is the saturated vapour pressure at 40°C., g weight of the water caught by calcium chloride tubes connected to the furnace, P atmospheric pressure, P' pressure of the introduced air, p saturated vapour pressure at T, T absolute temperature of B in Fig. 1, V volume of the introduced air, and M 18.

Table 1 shows the calculated results, from which it was confirmed that the air current had the saturated vapour pressure at the desired temperature. The experimental results of the dehydration and hydration of Odo acid clay between room temperature and 150°C. are shown in Tables 2–4 and Fig. 3, and those of the dehydration up to 800°C., in Tables 5–7 and Fig. 4.

Table 2.

Dehydration ($T_2 = 25$°C., 23.8 mm. Hg)			Hydration ($T_2 = 25$°C., 23.8 mm. Hg)		
T_1 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)	T_1 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)
35	50	0.80(×)	120	35	11.31
50	30	3.90	100	35	10.25
60	15	6.14	80	40	8.78
80	25	8.46	60	35	6.50
100	15	10.04	50	50	4.39
120	15	11.22	35	60	0.22
150	10	11.40			

Table 3.

Dehydration ($T_2 = 40$°C., 55.3 mm. Hg)			Hydration ($T_2 = 40$°C., 55.3 mm. Hg)		
T_1 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)	T_1 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)
50	50	0.72	120	35	10.68
,,	50	0.14(×)	,,	35	10.51
60	20	4.04	100	35	9.35
,,	30	3.96	,,	34	9.31
80	35	7.16	80	40	7.59
,,	35	6.96	,,	40	7.61
100	35	9.30	60	35	4.76
,,	25	9.16	,,	35	4.76
120	35	10.60	50	45	1.01
,,	35	10.34	,,	45	1.03
150	38	10.84			
,,	40	10.96			

Table 4.

Dehydration ($T_2 = 60°C.$, 149.4 mm. Hg)			Hydration ($T_2 = 60°C.$, 149.4 mm. Hg)		
T_4 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)	T_4 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)
70	25	1.03(×)	120	70	9.20
,,	35	0.76(×)	,,	90	9.22
80	60	3.24	100	40	9.27
,,	40	3.60	,,	50	7.28
100	20	6.78	80	65	3.62
,,	20	6.52	,,	85	3.81
120	20	8.90	70	70	0.44(×)
,,	40	9.20	,,	90	0.28(×)
150	25	10.11			
,,	25	10.34			

(×) Weight increase in %.

Table 5.

Dehydration (1.5 mm. Hg, Drying bottles ($CaCl_2$, H_2SO_4) instead of thermostat)					
T_4 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)	T_4 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)
35	30	4.50	150	20	11.68
			200	20	11.95
50	20	6.82	300	20	12.18
,,	24	7.10	,,	20	12.32
60	25	8.52	400	20	12.75
80	32	9.70	500	25	14.15
,,	30	9.59	,,	25	14.05
100	30	10.75	600	20	15.60
120	25	11.54	800	10	15.84
,,	25	11.46	,,	10	15.76

Table 6.

Dehydration ($T_2 = 25°C.$, 23.8 mm. Hg)					
T_4 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)	T_4 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)
50	20	3.99	400	15	12.66
100	25	10.12	500	15	13.70
150	15	11.37	600	15	15.24
200	15	11.70	800	15	15.58
300	15	12.24			

Table 7.

Dehydration ($T_2 = 40°C.$, 55.3 mm. Hg)					
T_1 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)	T_1 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)
100	20	9.28	400	30	12.39
,,	15	9.31	,,	30	12.51
,,	20	9.11			
150	30	10.78	500	25	13.33
,,	20	10.97	,,	30	13.59
			,,	25	13.23
200	40	11.21	600	25	14.65
,,	30	11.39	,,	25	14.83
,,	35	11.36			
300	45	11.84	800	20	15.36
,,	40	12.03	,,	15	15.34
,,	40	11.90	,,	20	15.45

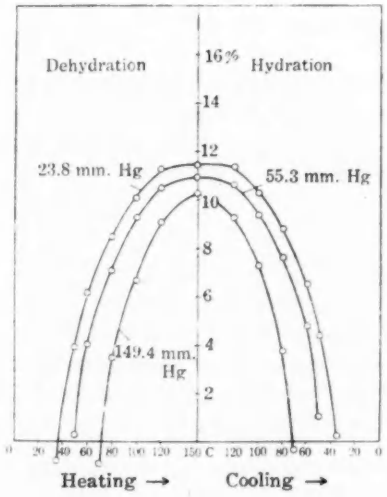

Fig. 3.

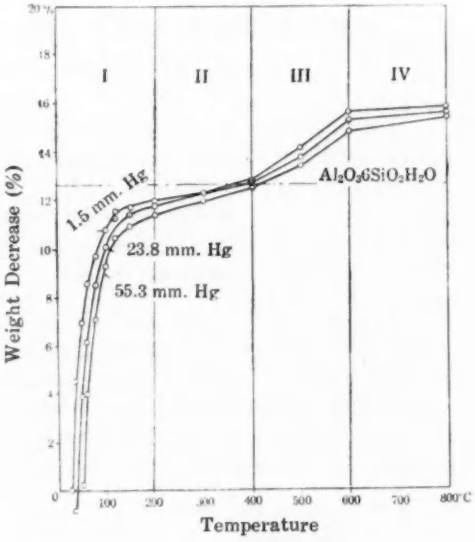

Fig. 4.

From the above investigations, it seems that the following conclusions must be derived: (1) There could not be observed the existence of a polyhydrate. (2) The water evolved on heating up to 300°C. is the adsorbed water and that evolved above 300°C. is the combined water. (3) The amount of the combined water nearly corresponds to one molecule of water, assuming that Odo acid clay has the composition $Al_2O_3 \cdot 6SiO_2$ in the anhydrous state.

In conclusion, the author wishes to express his sincere thanks to Prof. M. Matsui for his invaluable advices and to Prof. N. Sasaki for his kind guidance given throughout this work.

(November 30th, 1933)

Kanazawa Technical College,
Kanazawa, Japan.

ON THE ACTION OF LIGHT UPON THE DISSOLUTION OF AMORPHOUS SELENIUM IN CARBON BISULPHIDE.

By Jitaro SHIDEI, Shogo HASHIZUME, and Saburo KITAHARA.

Received April 2nd, 1935. Published August 28th, 1935.

The solubility of red amorphous selenium in carbon bisulphide and the action of light on it have been measured by several investigators.[1] Their results, however, are qualitative in nature. The present work was undertaken in order to determine these systematically and more accurately, for studies of this sort are valuable for the light they throw upon the dissolution of some materials sensitive to light.

Experimental. Red amorphous selenium was prepared by reducing selenium dioxide with sulphur dioxide in aqueous solution acidified with hydrochloric acid. The selenium dioxide was obtained by dissolving vitrious selenium of Merck in dilute nitric acid and purifying by repeated sublimation at about 300°C. in the atmosphere of nitrogen dioxide in a glass tube. Carbon bisulphide was carefully purified by the ordinary method.

(1) E. Mitscherlich, *Sitzber. Akad. Wien*, **1855**, 409; *J. prak. Chem.*, (1), **66** (1855), 257. C. F. Rammersberg, *Ber.*, **7** (1874), 667. R. Saunders, *J. Phys. Chem.*, **4** (1900), 455. G. Briegleb, *Z. physik. Chem.*, (A), **144** (1929), 340; *Naturwiss.*, **17** (1929), 51.

In every experiment, 250 c.c. of carbon bisulphide and 1 g. of red amorphous selenium were employed. Carbon bisulphide was previously kept in a reaction vessel at the required temperature, with which selenium was then mixed. The time at which the two components were mixed was taken as the initial point of dissolution. After mixing them, portions, each nearly 25 c.c., of the solution were withdrawn at proper time intervals and their compositions were determined.

For the light source, an electric lamp of 100 volts and 400 watts was employed, and the reaction vessel was illuminated from its bottom. The experiments were carried out at 33°, 25°, 0.5°, −9°, and about −60°.

(1) *The results at 33°C.* In the dark, the dissolved amount of selenium first increased rapidly and reached its maximum after about 2 hours. After that time, it decreased slowly, and in about 10 hours it seemed to reach a constant value. Previous to the time when the maximum was observed, a quantity of red monoclinic crystals was found to deposit on the bottom of the vessel, and after that time the residue was observed to consist entirely of red monoclinic crystals.

In the case of exposing to light, similar behaviours as in the dark were observed, but the rate of dissolution increased remarkably. The constant dissolved amount which was to be reached finally, seemed to coincide with that in the dark. The experimental results are shown in Table 1 and Fig. 1. The dissolved amounts are given in mg. Se per 100 g. CS_2.

Table 1.

Temp. °C.		Time (hours)									
		1	2	3	4	5	6	8	10	26	28
33	(D)	67.0	98.1	98.9	93.6	87.4	83.1	72.8	70.0	66.5	69.0
	(L)	99.5	99.2	—	79.4	—	71.6	68.8	67.2	60.5	60.1
25	(D)	17.4	33.8	—	63.9	—	65.9	59.9	56.5	—	48.0
	(L)	50.4	63.2	—	58.4	—	55.2	48.0	44.5	44.9	45.4
0.5	(D)	—	0.9	—	0.7	—	1.0	1.8	4.4	—	—
	(L)	21.6	24.3	—	28.3	—	26.9	26.4	25.5	—	—
−9	(D)	—	0.6	—	0.8	—	1.0	0.8	—	—	—
	(L)	17.4	22.4	—	23.4	—	18.6	18.3	—	—	—

(D) and (L) show the results in the dark and in exposure to light respectively.

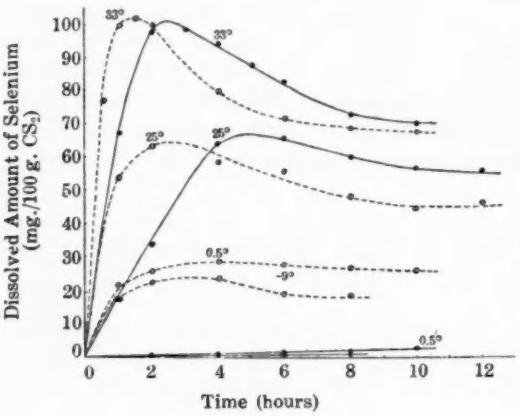

Fig. 1.

(2) *The results at 25°C.* In this case similar behaviours of dissolution were observed; the dissolved amount of selenium had a maximum value, and after a long time it seemed to reach a constant value smaller than that at 33°C. The red monoclinic crystals were also found depositing about the time of the maximum dissolution. However, the dissolved amount at each time was far smaller than that at 33°C., and both the time needed to reach the maximum and that to the final constant value were longer in this case than at 33°C. Light exerted more remarkable influence upon the rate of dissolution.

(3) *The results at 0.5°C. and −9°C.* In the dark, the dissolved amount of selenium was quite small and the rate of dissolution was so slow at these temperatures that the maximum dissolution was not reached within 10 hours. The action of light on the rate of dissolution was found to be very strong as will be seen from Table 1 and Fig. 1. At these temperatures red monoclinic crystals were found only in a trace and barely after exposure to light for about 6 hours, but not in the dark.

(4) *The results at about −60°C.* In the dark, the dissolution of selenium was not observed at all. By exposure to light, it was dissolved slightly.

Discussion of Results. G. Briegleb[1] has confirmed the constitutions of the several modifications of selenium and interpreted their transformation in solution by a diagram for pseudo ternary solution. According to him, the red amorphous selenium is pure Se_2, the monoclinic one is mixed crystals of varying compositions of Se_1 and Se_2, the latter predominating in amount, and the amorphous one is transformed into the monoclinic through the equilibrium $2\,Se_1 \rightleftarrows Se_2$ in solution, after being dissolved in carbon bisulphide.

The results obtained by the present writers seem undoubtedly in some degree to give a strong evidence in favour of the consideration of Briegleb. The above-mentioned fact that the dissolved amount of selenium has a maximum value, is in a good agreement with his view, for, according to it,

the deposition of the monoclinic selenium from the solution and the dissolution of the amorphous one must compensate each other after a certain time, and then, the former would predominate over the latter in rate. When all of amorphous selenium was transformed into the monoclinic one, the dissolved amount would reach a constant value corresponding to the solubility of the latter, as was the case in every experiment mentioned above except those at lower temperatures. In order to ascertain this again, the solubility of monoclinic selenium was measured in the dark. The samples used for this purpose were prepared by deposition from solutions of amorphous selenium in carbon bisulphide at the respective temperatures at which their solubilities were to be measured. The experimental results are given in Table 2 (No. 1 and No. 3).

Table 2.

Temp. °C.	No.		Time (hours)				
			1	2	4	6	8
33	1	(D)	42.6	53.0	62.1	64.4	65.0
	2	(L)	40.5	53.1	61.5	64.9	67.5
25	3	(D)	32.9	42.4	46.1	44.9	45.7
	4	(L)	32.8	41.2	46.2	45.9	45.2

The results indicate that monoclinic selenium has a definite solubility at each temperature and that, in favour of the consideration just mentioned above, the values of it coincide with those of the constant dissolved amounts given in Table 1, which were to be reached after a long time at the respective temperatures.

The transformation between the two modifications may also be considered to be due to some catalytic action of the solvent, but, the evidence of this cannot be shown in the present experiments.

Light seems to cause the increase in the rate of dissolution only. But, it cannot be decided from the results mentioned above, whether light acts on any one or both of the two modifications. In order to determine this, the following experiments were carried out. (1) The dissolved amounts of the samples of the monoclinic selenium the same with those used in No. 1 and No. 3 in Table 2 were measured at 33°C. and 25°C. and in exposure to light. The results obtained indicate no action of light on the monoclinic selenium as is shown in Table 2 (No. 2 and No. 4). (2) The dissolved amounts were measured with the mixtures the same with those employed in the experiment at 0.5°C. in Table 1 in the light and in the dark and at 0.5°C. By these experiments, it was found that the dissolved amount was suddenly decreased when the light was cut off, but increased again on exposure to light so as to reach the value which would be reached if the mixture were exposed to light

Table 3.

No.	Time (hours)										
	1	2	3	4	5	6	7	7.5	8	8.5	10
1	(L)				(D)						
	21.8	25.8	—	27.3	—	21.1	—	—	19.6	—	18.8
2	(L)	(D)									
	23.5	25.9	23.9	—	19.0	—	18.0	—	—	—	—
3	(L)				(D)				(L)		
	23.2	—	—	29.3	24.3	—	—	18.6	—	24.0	27.1

Table 4.

Time (hours)									
0.5	1	1.5	2	3	4	5	6	8	
—	99.5	—	99.2	—	79.4	—	71.6	68.8	[From Table 1, 33°C. (L).]
	(L)			(D)			(L)		
76.8	—	101.6	—	88.4	—	74.5	71.6	69.0	

throughout the time (Table 3). These behaviours can well be interpreted by assuming that light causes an increase in the rate of dissolution of the amorphous selenium alone, for, as has been already mentioned, at such a temperature as low as 0.5°C. some of the amorphous selenium remained unaltered for a fairly long time because of its slow transformation into the monoclinic modification. (3) Similar experiments were made at 33°C. These showed that the dissolved amounts in the light coincide with those in the dark at each time after the illumination of about 2 hours, as seen from Table 4. Since, in this case, the amorphous selenium was all found to transform into the monoclinic modification in a short time, the residue being all the monoclinic, it is a matter of course that the dissolved amount remains the same in the light and in the dark, provided the monoclinic modification does not suffer the action of light.

(December 15th, 1933)

Chemical Institute,
Tokyo University of Literature
and Science.

ON THE ACTION OF CHLORIDE FLUXES ON OXIDES CONTAINED IN ALUMINIUM.

By Takayasu HARADA.

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Introduction. The usual trouble experienced with aluminium ingot is the contamination or the formation of oxides. Hanson and Slater[1] attributed the chief cause of the formation of pin-holes in aluminium cast to the action of steam, and it is well known that in corroded parts of aluminium ware oxides are always detected in their centers. This being so, the injurious effect of oxides contained in aluminium is generally even more serious than that of other metals contained as impurities. The oxides in aluminium can not be removed by reducing agents such as carbon or hydrogen which are usually effective in other heavy metals. In the case of aluminium, however, it can only be cleaned or deoxidised by means of fluxes, but the fundamental chemical reactions underlying this action have never been fully elucidated so far.

I found that all the chloride fluxes have a decided cleaning power although in varying degrees, and that this deoxidising action is due chiefly to the chlorine gas liberated from these fluxes in contact with aluminium. Based on this knowledge, I made a systematic study of the action of chlorine gas and also of nitrogen gas on aluminium melt and was able to throw some light on the mechanism of cleaning.

Chloride Fluxing. As chloride fluxes the following chlorides were employed in my experiments: sodium chloride, potassium chloride, ammonium chloride, lithium chloride, calcium chloride, magnesium chloride, barium chloride, nickel chloride, manganese chloride, zinc chloride, aluminium chloride, ferric chloride, cupric chloride, stannous chloride, silicon tetrachloride, titanium tetrachloride, and carbon tetrachloride.

The aluminium ingot, 250 grams for each experiment, was melted at 700°C. in a graphite crucible, and each of the above fluxes in varying quantities packed in thin aluminium plate, was thrown into the melt kept at about 700°C. and pushed down to the bottom of the crucible by means of an iron utensil so that the deoxidising action was as complete as possible. Liquid

(1) *J. Inst. Metals*, **46** (1931), 187.

chlorides were injected to the bottom part of this melt through an iron tube and well agitated.

The molten aluminium acted upon by the fluxes was then cast. The specimen casts so obtained were then subjected to analysis and to metallographic examination.

It is certain, however, that all these chloride fluxes have more or less deoxidising power depending on the kind and quantity used. Moreover, the general effect appears about the same regardless of the kind of metals of the chlorides. The conceivable reactions which may occur between these chlorides and aluminium are discussed below.

Firstly, if the number of chloride molecules which decompose without entering into reaction with aluminium, either by heat, or by catalytic action of aluminium, or by some other causes, is taken as x, then

$$xM_aCl_b = axM + bxCl \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1).$$

where M denotes metal.

Secondly, if the number of chloride molecules which decompose and give off chlorine that combines with aluminium is taken as y, then

$$yM_aCl_b + cAl = cAlCl_3 + ayM \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2).$$

where $by = 3c$, hence $c = by/3$.

Lastly, if the number of chloride molecules which remain as such or go out of the sphere of reaction by sublimation or volatilisation, is taken as z, then

$$zM_aCl_b = zM_aCl_b \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3).$$

Although it is conceivable that a certain portion of the chloride forms double salts with aluminium or aluminate, such complex cases are not included in the formula (3) for the sake of simplicity. This omission, however, does not interfere much with the main discussion, for, as has been confirmed by experiments, no chloride remains in the cooled cast of aluminium.

From the above three equations we obtain

$$(x+y+z)M_aCl_b + (by/3)Al = (by/3)AlCl_3 + (ax+by)M + bxCl + zM_aCl_b \quad . \quad (4).$$

If there is no chloride that has not undergone decomposition, or in the case $z = 0$,

$$(x+y)M_aCl_b+(by/3)Al = (by/3)AlCl_3+(ax+by)M+bxCl \quad \ldots\ldots\ldots\ldots \quad (5).$$

Therefore, if we determine, after the treatment with a chloride, the amounts of M and Cl remaining in the aluminium and that of evolved chlorine, we can conjecture the type of the reactions which actually took place during fluxing.

For this purpose, the amount of chlorine liberated from the chloride thrown into aluminium was first determined, but it was soon discovered that the results obtained were not entirely reliable on account of several factors which made the determination very troublesome. Under the circumstances, the amount of metal remaining in the aluminium specimen was determined on one hand, and on the other hand the amount of chlorine liberated by the decomposition of the chloride alone in a heated tube at 800°C. was estimated. From the combined results of these determinations, the degree of decomposition of the chloride may be more accurately estimated.

A fixed amount of each of the above-mentioned chlorides was thrown into the molten aluminium in a graphite crucibles, and the chlorine gas evolved was absorbed by normal solution of silver nitrate, the amount of chlorine absorbed being determined by titrating the excess of silver nitrate with normal sodium chloride solution.

It must be mentioned that in order to obtain reliable figures in this experiment it is necessary to repeat the experiment at least 6 times—sometimes as often as 9 times—as it is exceedingly difficult to carry out the experiments under the same conditions exactly.

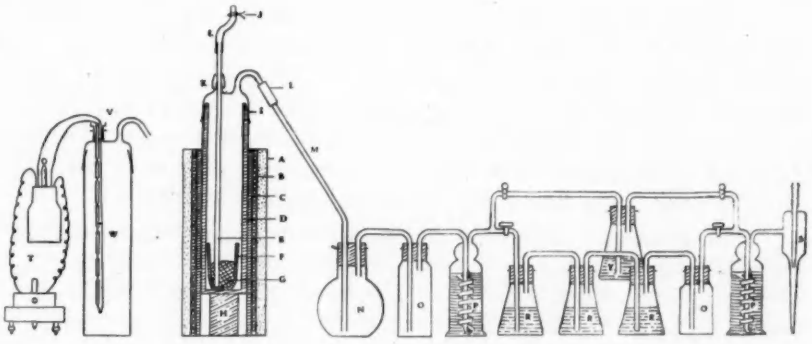


Fig. 1.

The arrangement of the apparatus for the experiment is shown in Fig. 1. A tall refractory cylinder with a closed bottom (D) is placed inside an electric

furnace (ABC) supported on a block (H) and the open end of the cylinder is covered tightly with a glass cap (I) provided with a hole and a branch pipe. The aluminium specimen (G) is melted in a graphite crucible (F) placed on the bottom of the refractory cylinder, and an iron pipe (E) passing through a hard rubber tubing (K), is inserted into the molten aluminium. A thick rubber tube (L) is attached to the top of the iron pipe and is provided with a regulating cock (J). The branch pipe of the glass cap is connected with a cooling tube protruding into a dust-catcher (N), which is followed by an empty bottle (O), a gas drying bottle (P) filled with concentrated sulphuric acid, bottles (R, R, R) containing normal silver nitrate solution, another empty bottle (O), and a washing bottle of sulphuric acid (P) connected with a filter pump (S). An extra bottle (Y) containing a known quantity of normal silver nitrate solution serves for determining the end point of the reaction by sucking a part of the gas through it toward the end of reaction. If no turbidity occurs in this bottle the reaction may be considered as finished. In the case when the degree of decomposition of a chloride alone is to be examined by putting it in a hot place heated at 800°C., a cylinder (W) instead of (D) is used in which a thermo-couple is placed, the other parts being the same as the above-mentioned arrangement.

A fixed amount of a chloride was thrown into the aluminium melt through the iron pipe (E) and the suction pump (S) was set to work, adjusting at the same time the cock (J) so that the absorption of the chlorine would be complete.

A great deal of attention is required for control of suction according to the nature of the chloride—whether it is volatile or fusible. Even volatile chlorides seldom reach as far as bottle (O) or (P) on strong suction, but are generally deposited in the cooling tube (M) and are mostly caught in the bottle (N). Three bottles of silver nitrate solution were found to be sufficient on actual experiment. No accident whatever occurred even in the case of liquid chloride. The results of experiments are given in Table 1.

From these results it will be noticed that the various chlorides differ in their decomposition rates. The following chlorides were found to give off a comparatively large quantity of chlorine: NH_4Cl, LiCl, $MgCl_2$, $ZnCl_2$, $MnCl_2$, $AlCl_3$, $FeCl_3$, $CuCl_2$, $SiCl_4$, and $TiCl_4$. It is interesting to note that the decomposition of LiCl and $FeCl_3$ is very much accelerated in the presence of aluminium. The following chlorides, on the other hand, suffer decomposition to a much less extent: NaCl, KCl, $CaCl_2$, $BaCl_2$, $NiCl_2$, $SnCl_2$, and CCl_4, of which NaCl alone is enhanced in its decomposition rate when it is in contact with molten aluminium.

Table 1.

Chloride		NaCl	KCl	NH_4Cl	LiCl	$CaCl_2$	$MgCl_2$	$ZnCl_2$	$BaCl_2$	$NiCl_2$	$MnCl_2$	$AlCl_3$	$FeCl_3$	$CuCl_2$	$SnCl_2$	$SiCl_4$	$TiCl_4$	CCl_4
Quantity of sample taken (g.)		5	5	5	5	5	5	5	5	5	5	5	5	5	5	10 (6.56 c.c.)	10 (5.69 c.c.)	10 (6.13 c.c.)
Quantity of Cl } in the Quantity of M } sample (g.)		3.033 1.967	2.388 2.621	3.316 1.684	4.181 0.819	3.150 1.850	3.725 1.275	2.686 2.314	1.455 3.545	2.737 2.263	2.878 2.122	3.985 1.015	3.279 1.721	2.629 2.371	1.825 3.175	9.45 0.54	7.498 2.51	9.21 0.79
Analysis	Quantity of Cl evolved (g.) Number of experiments	0.7551 9	0.2282 7	1.0250 6	2.8351 6	0.0825 6	1.5553 6	1.1784 6	0.0505 6	0.3703 6	1.0402 6	2.0204 6	1.0950 6	1.0404 6	0.4152 6	4.5704 6	3.5803 7	0.1203 6
	Quantity of M (g.) Number of experiments	0.4547 3	0.5392 3	nil. 2	0.4863 5	trace 3	0.5559 3	0.1240 4	nil. 3	0.4028 3	0.1033 3		0.5092 3	0.8962 4	0 8382 3	0.2360 3	0.1333 3	trace 2
Evolution rate of Cl (%)		15.1	5.8	20.5	56.7	1.7	31.1	23.6	1.0	7.4	20.8	40.4	21.9	20.8	8.3	45.7	35.8	1.2
Decomposition rate of Cl (%)		24.5	12.1	30.9	67.8	6 0	41.8	43.5	3.1	13.7	36.1	50.6	33.4	39.5	22.8	48.7	47.8	1.3
Decomposition rate of M (%)		28.2	20.4		59.3		43.6	53.5		17.8	49.4		46.5	37.8	26.4	43.7	53.0	
When the sample was thrown into an empty cylinder heated at 800°C.																		
Quantity of Cl evolved (g.) Number of experiments		0.3506 3	0.3225 5	1.0023 3	2.1052 5	0.8658 4	1.9401 3	1.4053 3	trace 3	0.5962 3	1.2448 3	2.9558 5	0.3153 5	1.6002 5	0.5303 3	8.3490 3	5.5244 3	0.0363 4
Evolution rate of Cl (%)		7.0	6.5	20.0	42.1	17.3	38.1	28.8	trace	19.9	24.9	59.1	6.3	21.2	10.6	83.5	55.2	0.4
Decomposition rate of Cl (%)		11.2	13.5	30.2	50.4	27.5	52.1	52.3		21.7	43.3	74.2	9.6	60.8	29.6	88.3	73.7	0.4

Decomposition seems to be accelerated by aluminium.
Considerable evolution of chlorine is noticeable. Such a chloride may be used as flux.
Remarkable evolution of chlorine is noted.
Very little evolution of chlorine. Such a chloride is unsuitable for flux.

Quantity of M (metal) = % of metal remaining in aluminium after reaction ÷ 100× Original quantity of aluminium. (It is assumed that the slag contained the same percentage of metal.)
Evolution rate of Cl (chlorine) (%) = Quantity of chlorine evolved ÷ Total weight of sample × 100.
Decomposition rate of Cl (%) = Quantity of chlorine evolved ÷ Total chlorine content in sample × 100.
Decomposition of M (%) = Quantity of metal estimated ÷ Total metal content in sample × 100.

Table 2. Analysis of the Original and Cleaned Aluminium Specimens.
(250 grams aluminium kept at 750C°. for 5–10 minutes after the flux is added.)

(A) Cleaning with Zinc Chloride.

Mark of sample	$ZnCl_2$ added (%)	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)	Zn mean (%)	Zn lost* (%)
0	Original Al ingot	1.010 1.672 1.918 2.589 2.213 3.356	0.73	0.36	0.127	
Z8	8	0.435 0.461 0.714 0.724 0.767	0.76	0.21	3.71	0.53
Z7	5	0.582 0.459 0.468 0.403 0.802	0.75	0.26	2.20	0.16
Z6	3	0.863 0.978 0.854 1.002 1.008	0.75	0.18	1.34	0.13
Z5	2	1.063 0.975 1.065 1.927 0.726	0.77	0.21	0.92	0.10
Z4	1	0.828 0.769 0.584 0.813 0.848	0.71	0.25	0.51	0.07
Z3	0.7	0.844 0.939 0.904 0.794 0.703	0.72	0.24	0.4005	0.005

(A) (*Concluded*)

Mark of sample	$ZnCl_2$ added (%)	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)	Zn mean (%)	Zn lost* (%)
Z2	0.5	0.728 0.659 0.808 0.798 0.798	0.71	0.26	0.294	0.023
Z1	0.3	0.988 0.898 0.924 1.078 0.918	0.69	0.23	0.178	0.050

*Zn in aluminium ingot + Zn in $ZnCl_2$ added −Zn in cleaned aluminium.

(B) Cleaning with Titanium Chloride.

Mark of sample	$TiCl_4$ added (g.)	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)	Ti mean (%)
T4	10	1.231 1.751 0.945 0.932	0.89	0.37	0.45
T3	5	1.722 2.430 0.752	0.80	0.34	0.26
T2	3	1.636 1.218 0.513 1.556	0.78	0.30	0.14
T1	1	2.165 1.020 2.051 1.644	0.73	0.36	0.06

Taking the rate of chlorine evolution into consideration the following chlorides may be recommended as suitable fluxes for the evolution of chlorine: LiCl, $AlCl_3$, $FeCl_3$, $SiCl_4$, and $TiCl_4$.

Now returning to the subject of the cleaning or deoxidising action of the chloride, it can be supposed that this is attributable to the action of either the chloride, i.e. M_aCl_b itself, or the products of decomposition, i.e. M or Cl, or $AlCl_3$ newly formed.

For example in the case of zinc chloride used as a flux, it is not likely that $ZnCl_2$ itself or $AlCl_3$ formed will reduce Al_2O_3. Besides, in the cleaned aluminium, chlorine is not detected. It is also not expected that the metallic zinc would have a deoxidising action on aluminium. Chlorine, on the other hand, is entirely non-reactive with the oxygen in aluminium, and yet the fact that cleaning has been effected is evident from the analytical results recorded in Table 2 (A). Similarly, titanium tetrachloride has also a cleaning power as shown in Table 2 (B).

Here again, the cleaning action can not be ascribed to any chemical reaction in connection with $TiCl_4$ and aluminium. It is interesting to note that the cleaning action is not necessarily proportional to the amount of the flux added, and that in the case of zinc chloride, about 0.7% of the flux gives the maximum efficiency or the condition approaches the case of equation (5) in which no chloride remains undecomposed. This percentage of flux for the maximum efficiency, however, varies with the nature of chlorides, the quality of the aluminium, and the amount of the melt.

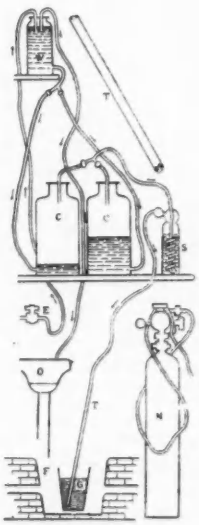


Fig. 2.

Based on the results of the above experiments, that all the chlorides show more or less a similar cleaning effect, the present author was led to think that the chlorine gas set free from the chloride may perhaps be responsible, directly or indirectly, for this deoxidising action. He, therefore, conducted experiments by using chlorine gas alone in an apparatus as shown in Fig. 2.

Chlorine gas, prepared from hydrochloric acid and potassium permanganate, is stored in bottles (C, C). By means of a water flow from a reservoir (W), whose water level is kept constant by an overflow device, the chlorine gas, after being dried over sulphuric acid (S), is bubbled, at a constant rate through an iron pipe (T) having many small holes at one end,

into the molten aluminium in a graphite crucible (G). N in the figure is a nitrogen bomb, and in case nitrogen gas is used instead of chlorine gas for comparison, this bomb is directly connected to the drying bottle (S).

The results of experiments, in which chlorine gas was passed into 250 grams of aluminium melt at 750°C. for varying durations are shown in Table 3.

Table 3. Analysis of Aluminium Treated with Chlorine Gas.
(250 g. Al treated at 750°C., settled for 5–10 min. after the gas passed.)

Mark of sample	Duration of passing of chlorine	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)	Mark of sample	Duration of passing of chlorine	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)
0	See Table 2 (A)				C5	1 min.	0.987 0.718 0.807 0.908 0.870	0.74	0.11
C1	10 sec.	1.235 1.261 1.088 1.062 0.918	0.65	0.11	C6	1.5 min.	0.707 0.897 0.953 0.938 0.784	0.80	0.11
C2	15 sec.	1.005 1.023 1.215 1.061 0.889	0.68	0.17	C7	2 min.	0.717 0.879 0.824 0.791 0.850	0.96	0.23
C3	20 sec.	1.173 0.708 1.016 0.898 1.036	0.73	0.25	C8	2.5 min.	0.736 0.795 0.838 0.848 0.760	0.89	0.19
C4	40 sec.	0.774 0.671 0.634 0.987 0.870	0.79	0.11					

As obvious from these results, the chlorine gas alone is decidedly effective for the cleaning action, and the Al_2O_3 content approaches the level of what may be called the "limit of dissolved oxygen" with the prolongation of the treatment. By this treatment, aluminium is attacked by chlorine and some portion is lost as aluminium chloride.

Table 4. Ignition Temperatures of Various Metals in Chlorine Gas. (Sample taken, 5 grams.)

Metal	Ignition temp. °C.	Extinction temp. °C.	Duration of burning. (min. per 5 g.)
Aluminium	130	270	10
Iron	215	315	8
Silicon	440	510	22
Copper	370	380	0.5
Zinc	535 (390*)	560	30

*White fume was observed, but no active ignition occurred at this temperature.

Table 4 shows the ignition temperatures of aluminium and other metals generally contained in aluminium as impurities in the atmosphere of chlorine, as determined by the author. The same table also shows the extinction temperatures and the duration of burning when 5 grams of each of the specimens were employed for the experiment. As all the metals, contained as impurities, have a higher ignition and extinction

Table 5. Analysis of Aluminium Treated with N_2 Gas. (250 g. Al treated at 750°C., and settled at the same temperature for 5–10 min. after the passing of the gas.)

Mark of sample	Duration of passing of nitrogen	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)	Mark of sample	Duration of passing of nitrogen	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)
0	See the Table 1.				N5	1.5 min.	0.823 0.624 0.775 0.598 0.971	0.50	0.14
N1	10 sec.	1.423 1.388 1.298 0.663 1.617	0.53	0.15	N6	2 min.	0.818 0.633 0.597 0.729 0.659	0.70	0.13
N2	20 sec.	0.938 0.808 0.908 1.834 1.157	0.53	0.14	N7	3 min.	0.838 0.904 0.623 0.728 0.673	0.65	0.13
N3	40 sec.	0.812 0.595 0.588 0.938	0.51	0.15	N8	4 min.	0.938 0.668 0.790 1.099 0.826	0.65	0.12
N4	1 min.	0.838 0.903 0.958 0.724 0.625	0.44	0.14	N9	5 min.	0.893 0.838 0.725 0.753 0.828	0.67	0.12

temperatures than pure aluminium, they are not materially reduced in quantity by the treatment with a chloride.

During this treatment, the formed chlorides, the oxides, and other occluded impurities accumulate on the top of the melt and go into the slag, which amount increases with the duration of the treatment. By analysis, the cleaned aluminium was found to contain almost no detectable chlorine. As has already been confirmed, chlorine gas has no deoxidising action. Hence, the only possible explanation regarding the cleaning effect by chlorine must be sought mainly in its action of mechanical removal of the oxide at the time of its ascension through the molten aluminium. It is also conceivable that the undecomposed chloride or the newly formed aluminium chloride aids the removal of the impurities at the time of their sublimation or volatilisation.

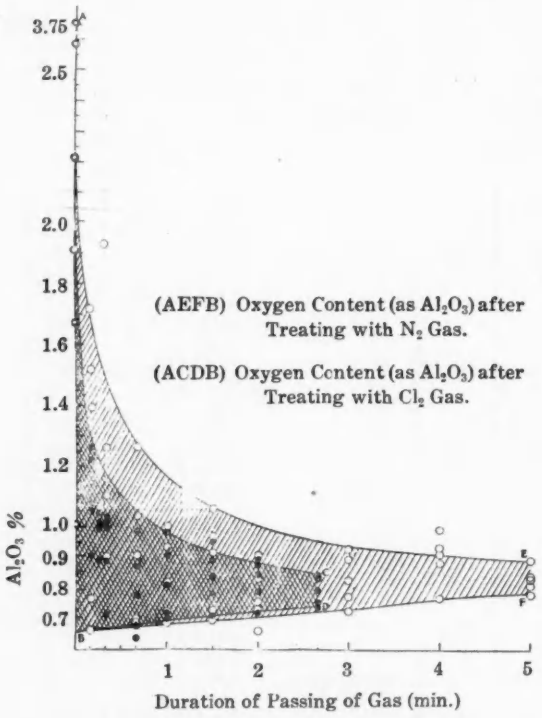
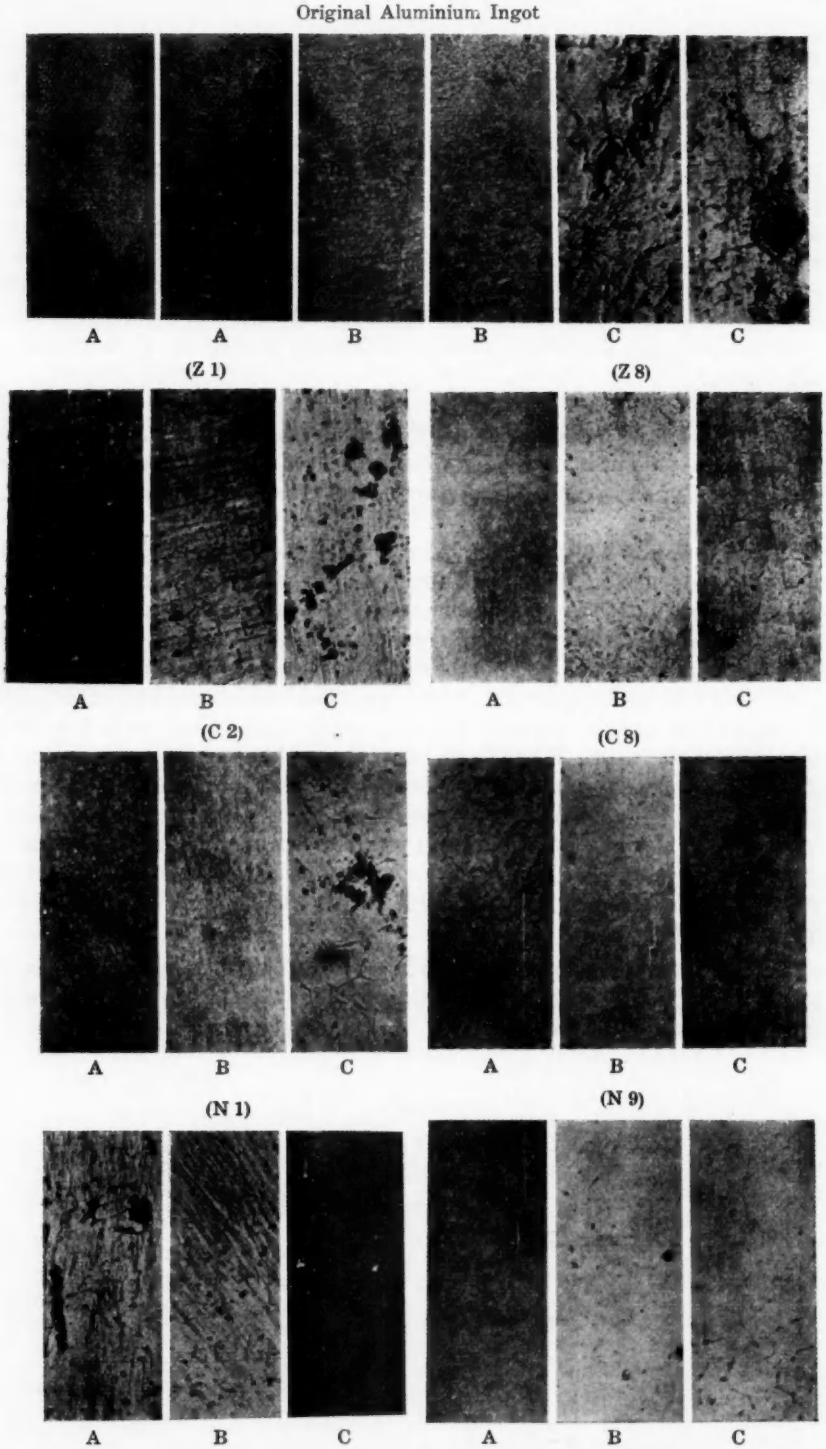


Fig. 3.

If the above reasoning be correct, any kind of gas, which has no tendency to remain in aluminium as chlorine, should act in the same way. In order to test this point, I tried in a similar way with nitrogen gas for comparison, which has been found almost non-reactive with aluminium. The results of experiments with nitrogen gas are given in Table 5, which shows clearly that the above reasoning is justified.

The cleaning effect of chlorine and nitrogen is shown diagrammatically in Fig. 3; this indicates clearly that similar, if not the same, results are obtained with these gases.



A: Macrograph ×7, B: Polished surface ×120, C: Surface etched with NaOH solution.

Fig. 4.

From the above experimental results, the author ventures to propose that any gas that is not likely to be occluded in aluminium or any compound which will liberate such a gas in molten aluminium would act as a cleaning agent. Its cleaning efficiency, however, depends on such properties as viscosity between the gas and the metal, specific gravity of the metal, etc. For a chloride flux, it is, therefore, advisable to select a compound which decomposes easily according to the equation (1) and the liberated metal, when alloyed with aluminium, does not harm the properties of the resulting aluminium.

Microscopical Examination of the Specimens. All the specimens obtained in the present investigation were microscopically examined. In Fig. 4 photographs of some representative specimens are shown.

Conclusion. When aluminium ingot is treated with chloride fluxes, the content of oxygen in the aluminium is decreased. The cleaning action of these chloride fluxes is mainly due to the chlorine gas liberated from the chlorides, which, when escaping from the aluminium melt, conveys and removes the oxide and other impurities contained in the aluminium melt. Any other gas, such as nitrogen, which is not likely to be combined or occluded by aluminium, has also the same cleaning power if used alone or in combination with other gases. When fluxes other than chlorides have to be employed for cleaning purpose, one should select such compounds which do not remain unchanged in the aluminium or as their decomposition products. Or if they remain, they should give no harmful effect to the aluminium. Compounds that give off a comparatively large quantity of harmless gas in aluminium are suitable for cleaning fluxes, and LiCl, $AlCl_3$, $TiCl_4$, and $SiCl_4$ are recommended for this reason.

The author might take this opportunity to say that cleaning by chlorine gas is actually carried out in several aluminium works in this country, and is giving satisfactory results.

(July 20th, 1934)

ON THE ARRANGEMENTS OF THE MICRO-CRYSTALS IN LEAD DEPOSITED BY ELECTROLYSIS.

By Hideki HIRATA, Yoshio TANAKA, and Hisaji KOMATSUBARA.

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Introduction. By way of continuity with our previous investigations[1] on the crystalline structure in various electro-deposited metals, essentially the same experiment has been repeated with electrolysed specimens of lead. The heterogeneous X-rays emitted from the molybdenum anticathode were also utilized in the present experiment.

Here it should be stated that the crystal form of lead belongs to $I''c$ of $a_0 = 4{,}983$Å.[2]

Specimens. To prepare the specimens used in this experiment, a platinum wire was steeped by 2 cm. into the electrolyte as the cathode. At a distance of 3–5 cm. from the cathode, a thin plate of lead, 1.5 cm. × 3 cm. in area and serving as anode, was placed. The conditions under which these specimens were obtained, are given in Table 1.

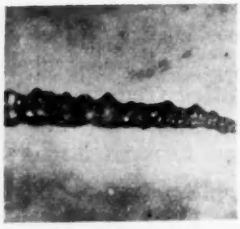
Table 1.

No. of specimens	Composition of electrolyte	Current of electrolysis (amperes)	Potential applied to the electrodes (volts)	Distance between the electrodes (cm.)	Temp. °C.
A	6 g. $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ was dissolved in 200 c.c. H_2O. $C_2H_4O_2$ sufficient for clearing the solution was added.	The current was gradually increased from about 0.1 ampere, with the augment of deposit.	4	5	about 20
B	10 g. $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ 5 c.c. $C_2H_4O_2$ 195 c.c. H_2O	0.1	3.5	3	20
C	5 g. $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ 2.5 c.c. $C_2H_4O_2$ 197.5 c.c. H_2O	0.1	3.5	3	20
D	2.5 g. $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ 1.3 c.c. $C_2H_4O_2$ 198.7 c.c. H_2O.	0.08	4	3	14

(1) For example, H. Hirata and Y. Tanaka; *Mem. Coll. Sci., Kyoto Imp. Univ.*, A, **17** (1934), 143.

(2) E. A. Owen and G. D. Preston, *Proc. Phys. Soc.*, **35** (1923), 101.

Though powdery or needle-shaped deposits of lead were often detected at the beginning of the electrolysis, the specimens of lead which appeared after several hours, usually had a foliated form with many branchlets. But some of the needle-shaped specimens were observed to remain unaltered, when electrolysis proceeded for a comparatively long time. The micro-structures of these two types of specimens are reproduced in Fig. 1 and 2.



Specimen C (needle-shaped). ×50.

Fig. 1.

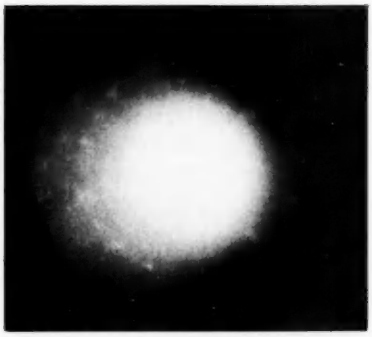
Specimen C (foliated). ×50.

Fig. 2.

Experimental Results. The crystalline structures of the specimens mentioned above were examined by means of Laue's method. To take a diffraction pattern of the foliated specimens, a piece of them was so placed that the foliated surface was perpendicular to the incident X-ray beam, while, with a fragment of the needle-shaped specimens, the interference figure was obtained by setting its longitudinal axis perpendicular to the direction of the incident beam. In doing so, the photographic plate was always placed perpendicularly to the incident beam in a position 3.2 cm. behind the specimen.

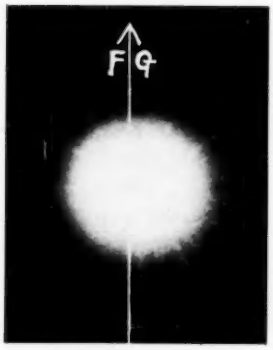
Some of the diffraction patterns thus obtained with the foliated and needle-shaped specimens are reproduced respectively in Fig. 3, 4, 5, 6, and 7. In these figures, the direction of the maximum growth of deposited lead (i.e., the direction of the longitudinal axis or the stem of the foliage) is represented by an arrow G.

Not only the patterns here reproduced, but also most of the diffraction figures given by these specimens, were found to be essentially the same: i.e., all the figures, except Fig. 3 were observed to be made up with a set of radiating bands. On the other hand, Fig. 3 consists of several Debye-Hull rings due to the reflections of the prominent atomic planes of the lead crystal. This shows that a considerable portion of the specimen giving Fig. 3, is composed of an irregular aggregation of microcrystals of lead, but the other specimens are mostly of a fibrous structure.



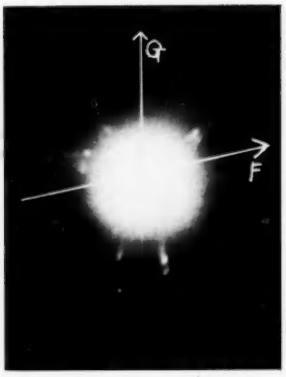
Specimen C (foliated). $\beta = 90°$.

Fig. 3.



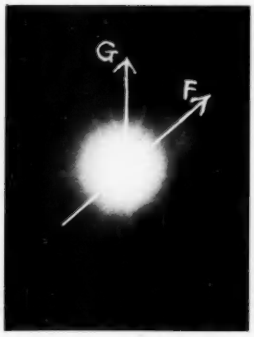
Specimen C (needle-shaped). $\beta = 90°$.

Fig. 4.



Specimen C (foliated).
$\beta = 90°$.

Fig. 5.



Specimen B (foliated).
$\beta = 90°$.

Fig. 6.

Specimen A (foliated).
$\beta = 90°$.

Fig. 7.

Having thus ascertained these facts, the writers tried to determine the direction of the common axis of the micro-crystals in the fibrous specimens mentioned above. This was done in the same manner as in our previous investigations.[1]

In the annexed figures, Fig. 8, 9, 10, and 11, the full lines represent diagramatically the theoretical positions of the prominent radiating bands, which are expected to appear when a lead crystal is rotated around a direction parallel to one of its [211] axes (represented by an arrow F), and the incident X-ray beam is made to strike this crystal taking the

direction perpendicular to the axis of rotation mentioned above. The shaded parts of the same figures are copies of the original plates of Fig. 4, 5, 6, and 7.(3) To transcribe these copies, the original plates of Fig. 4, 5, 6, and 7 were respectively placed upon Fig. 8, 9, 10, and 11, in such a way that the direction represented by F and the centre of the central spot in both figures coincide with each other. As can be seen from Fig. 8, 9, 10, and 11, the agreement between the calculated curves and those observed is satisfactory. Consequently, we may infer that the specimens giving the diffraction patterns reproduced in Fig. 4, 5, 6, and 7 are, in the main at least, composed of micro-crystals having one of the [211] axes in common.

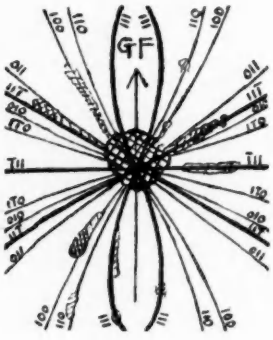


Fig. 8.

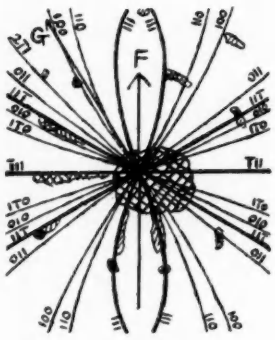


Fig. 9.

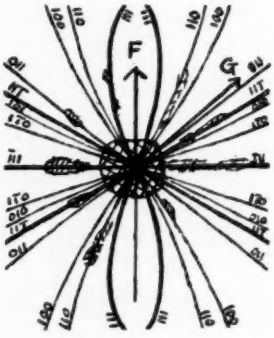


Fig. 10.

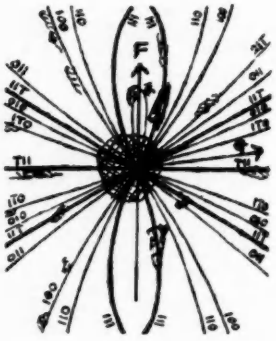
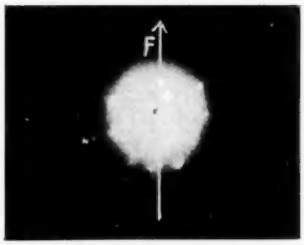


Fig. 11.

(3) It is to be noticed that the diffraction patterns reproduced in Fig. 3–7 and 12 interchange from right to left as compared with those of the original plates.

Next, to confirm the above inference, the writers investigated the interference phenomena due to an oblique incidence of the X-ray beam to the fibrous direction of the same specimen as was used in the case of Fig. 4. Fig. 12 is the diffraction figure taken when the axis of fibre was tilted 45° from its vertical position towards the incident beam. To take this diffraction figure, the photographic plate was also placed 3.2 cm. behind the specimen.



Specimen C (needle-shaped).
$\beta = 45°$.

Fig. 12.

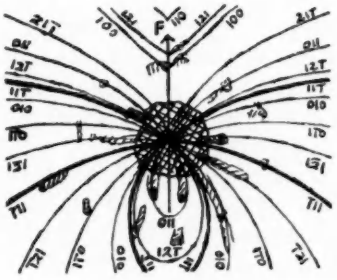


Fig. 13.

In the annexed figure, Fig. 13, the theoretical curves traced out by calculation are compared with Fig. 12. As may be seen from Fig. 13, the agreement between the calculated curves and the observed ones is rather satisfactory. Accordingly, our foregoing inference was confirmed as correct, and we may conclude that the micro-crystals of lead have a tendency to be electrolytically deposited with the normals to their icositetrahedral faces (211) arranged parallel to a definite common direction. This is in no way different from the experimental results given by Frölich, Clark, and Aborn.[4]

But, it is noticed that the direction of fibre thus determined, does not always coincide with the direction of maximum growth of deposited lead. As has already been seen, the diffraction patterns, Fig. 4, 5, 6, and 7, were produced, when the directions, represented respectively by F and G, were parallel to the photographic plate. Consequently we may conclude, on the one hand, that these two directions F and G coincide with each other in the needle-shaped specimen, which produced Fig. 4, while, on the other hand, both directions F and G being situated parallel to the largest surface of the foliated specimen, the angles between them are found by measurement from Fig. 5, 6, and 7 to be about 33°, 48°, and 80° respectively.

(4) *Z. Elektrochem.*, **32** (1926), 295.

The angles between the [211] axes of a crystal belonging to the cubic system, are generally confirmd by calculation to be 33°34′, 48°12′, 60°, and 80°24′. Thus, it may be inferred that the direction of the maximum growth of deposited lead G also coincides roughly with one of the [211] axes of the micro-crystals forming the considerable part of the specimens. This inference may explain why the branchlets of the foliated specimen make angles of about 33°, 48°, and 60° with one another, as shown in Fig. 2.(5)

Summary. The arrangements of the micro-crystals in electrolytic specimens deposited from acetic acid solutions, were examined with X-rays, by the so-called "transmission method". From the diffraction patterns obtained, it was confirmed on the one hand, that the micro-crystals of lead have a tendency to be electrolytically deposited in a fibrous way, with one of the normals to their (211) faces arranged parallel to a definite common direction, as was the case in the experiments of Frölich, Clark, and Aborn. On the other hand, the direction of the growth of deposited lead, was found to coincide roughly with any one of the [211] axes, which make an angle 0°, 33°34′, 48°12′, and 80°24′ respectively with the common axis of the micro-crystals.

In conclusion the writers wish to express their best thanks to Professor D. Uno for the interest he has taken in the experiments. Their thanks are also due to the Imperial Academy of Japan for the fund granted for the investigation.

Institute of Metallography,
Imperial University of Kyoto.

(September 25th, 1934)

(5) As all the branchlets of the foliated specimens were found not to lie in the same plane, the writers were obliged to flatten each specimen by placing it between two glass plates, before its micro-photograph was taken. Thus, the angles between some of the branchlets, especially those between the big branchlets and the stems of the foliage seen in Fig. 2, are different from the actual angles.

DIE DILATOMETRISCHEN UNTERSUCHUNGEN DER GEGOSSENEN KUPFERREICHEN BRONZEN.[1] (UNTERSUCHUNGEN ÜBER DIE FESTELÖSLICHKEIT DER LEGIERUNGEN. II.)

Von Denzo UNO, Saburo KATORI und Masamichi FUJII.

Eingegangen am 10. Mai, 1935. Ausgegeben am 28. August, 1935.

Allgemein ist das Feingefüge kupferreicher Mischkristall-Legierungen im gegossenen Zustand stark ausgeseigert. Insbesondere ist diese Neigung desto grösser, je länger das Erstarrungsintervall ist. In diesem Falle werden die Eigenschaften durch die ganzen Teile der Probe ungleichmässig, und wenn die unter Seigern verursachte zweite Phase spröde wäre, würden die mechanischen Eigenschaften der ganzen Probe verschlechtert. Soweit es möglich ist, muss man dementsprechend das Gefüge der Probe durch die richtigen Wärmebehandlungen homogenisieren.

Beim Homogenisieren wird die Probe oftmal überhitzt, oder sie wird der ungenügenden Erhitzung wegen länger Zeit wärmebehandelt. Es tritt also die Verflüchtigung des Bestandteiles, oder die Oxydation der Probe ein. Es wäre auch ökonomisch nicht wünschenswert.

Wir berichteten schon über die abnormen Dilatationserscheinungen,[2] welche die Gefügeänderungen beim Erhitzen der gegossenen Mischkristall-Legierungen begleitet.

Nun wurden in diesem Versuche die abnormen Dilatationsänderungen unter den verschiedenen Wärmebehandlungen gemessen. Es wurden dann die Beziehungen zwischen dieser Dilatations- und der Gefügeänderung bei den gegossenen kupferreichen Bronzen genau erläutert. Über die abnormen Ausdehnungserscheinungen der sandgegossenen Bronzen sind einige Versuche durch Imai u. Hagitani[3] schon berichtet worden.

Zum Dilatationsversuche benutzten wir die verbesserte Differential-Dilatometer[2] und die Messung wurde um sich vor Oxydation der Probe zu schützen, immer im Vakuum vorgenommen.

(1) Vorgetragen auf der Jahresversammlung der Japanischen Chemischen Gesellschaft, Tokio, April 1933.

(2) D. Uno, S. Yoshida u. S. Katori, vorgetragen auf der Versammlung des Chemischen Instituts kaisl. Universität Osaka, Juni 1931. Vortragssammlung desselben Instituts, **3** (1932), 152.

(3) Imai u. Hagitani, *Mem. Ryojun Coll. Engineering*, **4** (1931), 99.

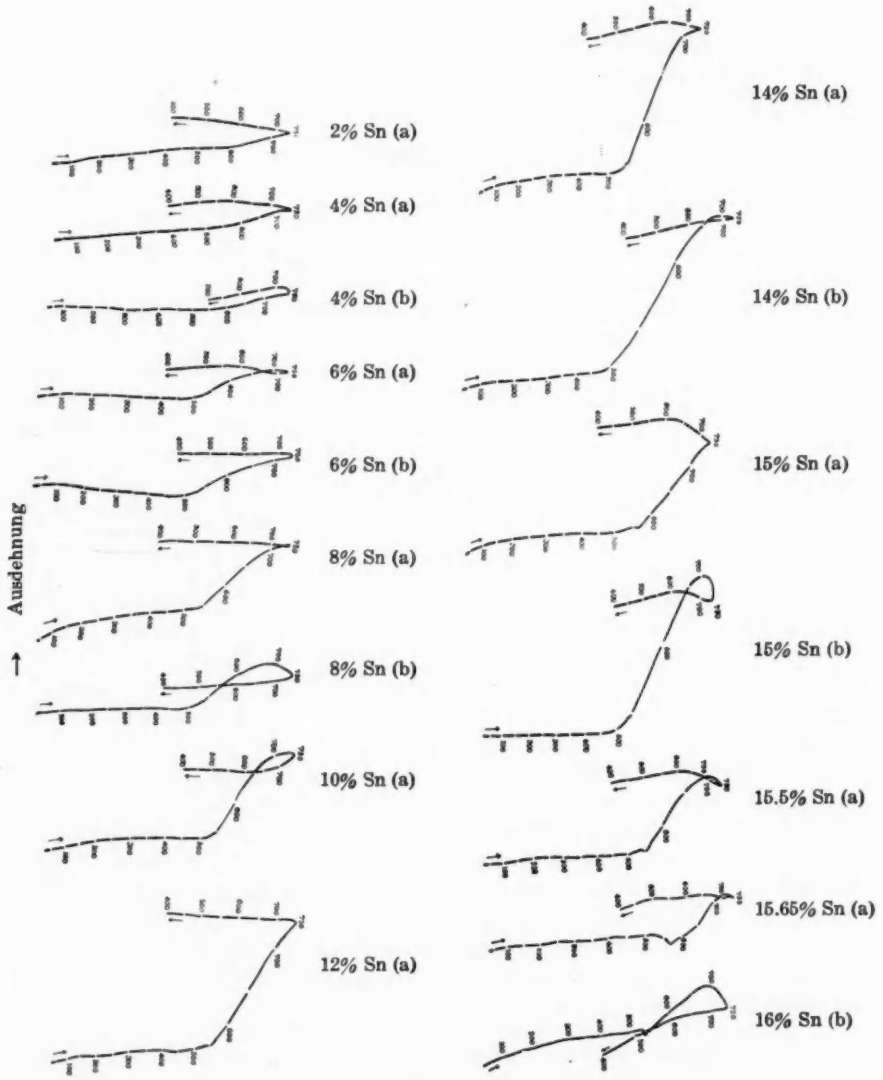


Abb. 1. Differentiale Dilatationskurve der gegossenen Bronzen.
(Gussform a u. b)

Abb. 1 zeigt die Wiedergabe der dilatometrischen Kurve von gegossenen Proben, die 2 bis 10% Zinn enthalten. Beziehungsweise entsprechen die Kurven a und b in Abb. 1 derjenige der im Kokillform a und b gegossenen Proben. Bei etwa 500°C. findet die abnorme Ausdehnung in den Proben statt, die über 4% Zinn enthalten. Je mehr Zinngehalt, desto grösser wird die Ausdehnung. Über 15% Zinn wird sie aber viel kleiner. Dies stimmt hauptsächlich mit den Ergebnissen von Imai u. Hagitani überein.

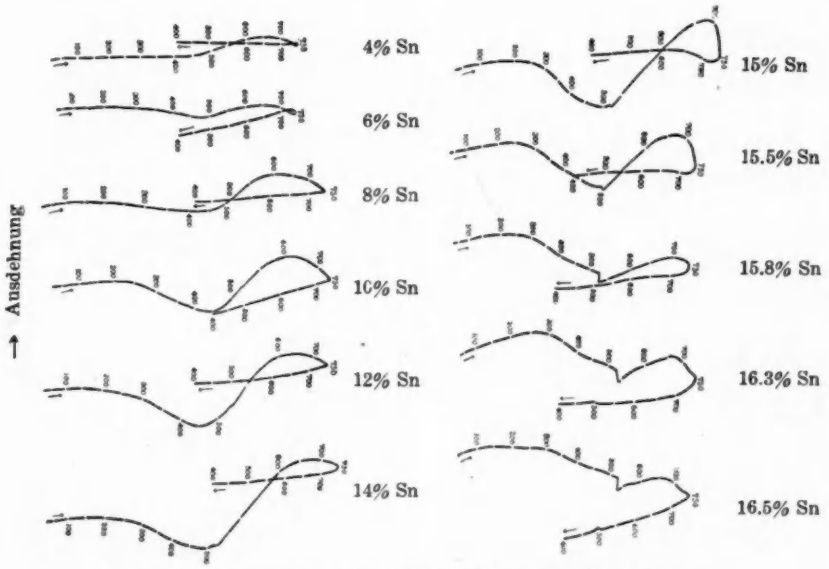
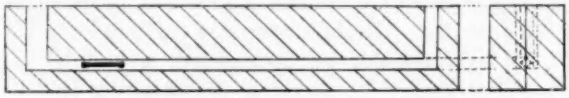


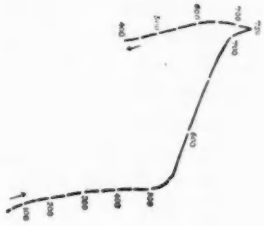
Abb. 2. Differentiale Dilatationskurve der gegossenen Bronzen. (Gussform h)

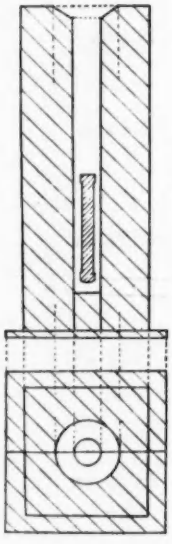
Abb. 2 ist die Wiedergabe der Kurve von den im Kokillform h gegossenen Proben, welche 4 bis 16% Zinn enthalten. Die Kurvengestalt ist etwas anders wie bei Abb. 1. Es zieht sich zum Beispiel von etwa 250°C. allmählich zusammen, und bei etwa 450°C. dehnt es sich aus. Nur findet sich diese Zusammenziehung über 10% Zinngehalt statt, und bei etwa 525°C. erscheint die Dilatationsänderung, welche dem eutektoidischen Horizontale entspricht, stark von ca. 16% Zinngehalt ab.

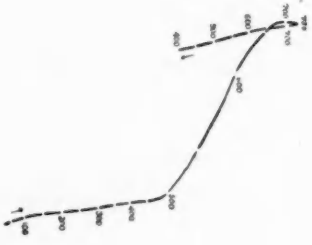
Es wurde nun bei den in die verschiedenen Gussform gegossenen Proben dilatometriert, welche 14% Zinn enthalten und die stärksten Aus-



(a) Fe-Kokill bei 250°C.



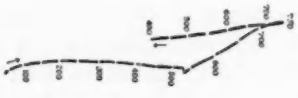




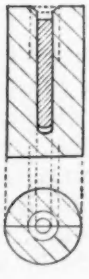
(b) Fe-Kokill bei −7°C.

(c) Fe-Kokill bei 20°C.

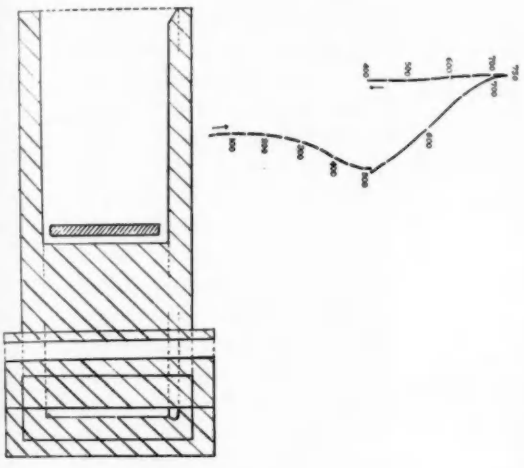
(d) Fe-Kokill bei 20°C.



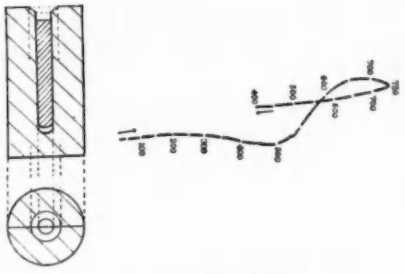
(e) Fe-Kokill bei 20°C.



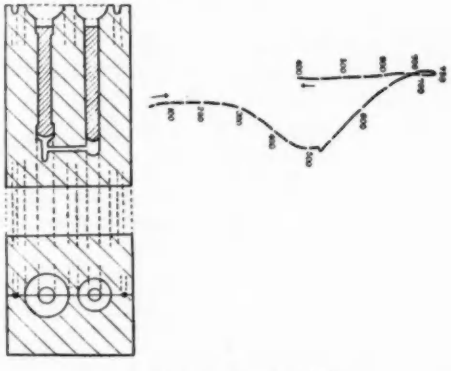
(f) Fe-Kokill bei 20°C.



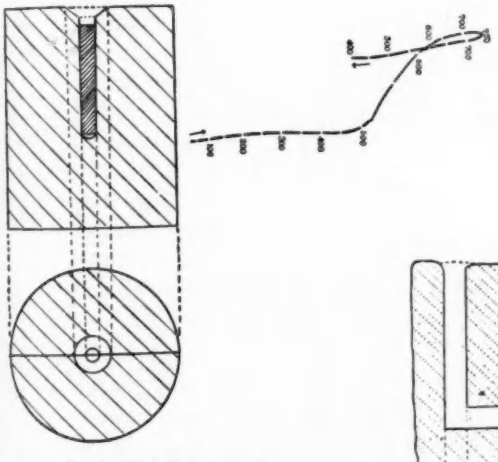
(g) Fe-Kokill bei 20°C.



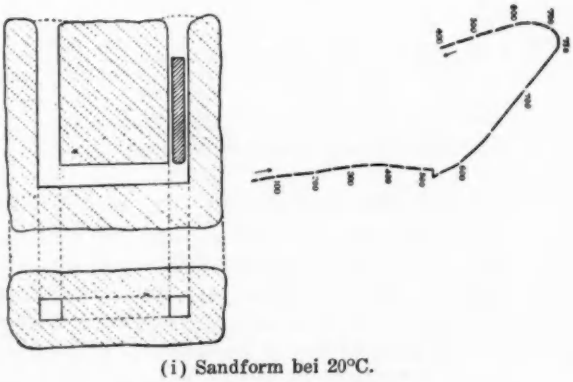
(j) Cu-Kokill bei 20°C.



(h) Fe-Kokill bei −7°C.



(k) Cu-Kokill bei 20°C.



(i) Sandform bei 20°C.

Abb. 3. Verschiedene Gussform und entsprechenden Dilatationskurve bei 14%-zinnhaltigen Bronzen.

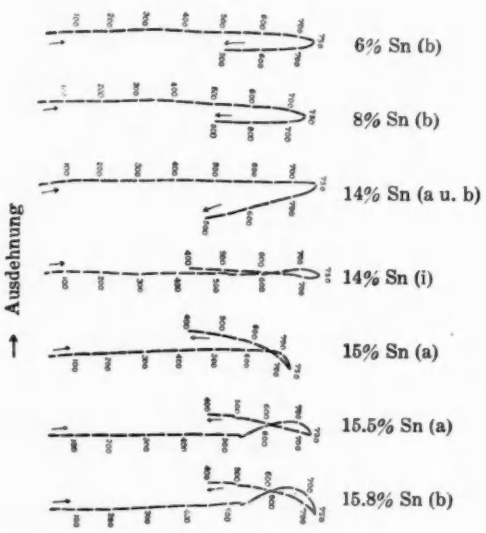


Abb. 4. Differentiale Dilatationskurve der ausgeglühten Bronzen.

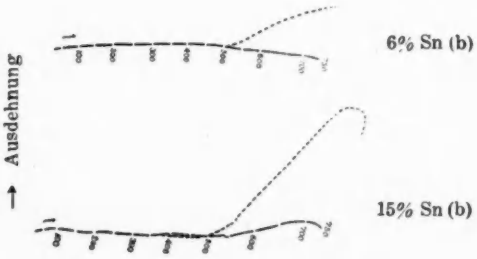


Abb. 5. Differentiale Dilatationskurve der abgeschreckten Bronzen.

dehnung besitzen. In Abb. 3 wurde der Vergleich zwischen den verschiedenen Gussformen und den entsprechenden Dilatationskurven versucht. Wie man sieht in Abb., findet die Ausdehnung bei tieferen Temperaturen statt, wenn die Kühlwirkung der Gussform zunimmt. Beispielsweise tritt in der Kurve der Proben k, j und b die Ausdehnung ein, schon bei etwa 500°C., welche unter grösseren Kühlwirkung gegossen wurden; aber bei etwa 650°C. hört sie auf. Die Ausdehnung setzt im Gegenteil bei höheren Temperaturen d. h. über 550°C. ein, bei der sandgegossenen Probe i, welche weniger Kühleffekt besitzt, und über 750°C. liegt ihr Endpunkt. Es liegt bei anderen Proben der Dilatationseffekte in der Mitte zwischen den obenbeschriebenen beiden Fällen.

Wie in Abb. 4 setzt bis 15% Zinngehalt die abnorme Ausdehnung nicht ein, bei Wiedererhitzung der einmal dilatometrierten Proben. Man kann nun vermuten, dass diese merkwürdige Ausdehnung beim Dilatometrieren der gegossenen Proben auf der Normalisierung der Gussgefüge, nämlich der Diffundierung der Gefügebestandteile beruht. Es wurden wie in Abb. 5 die abgeschreckten Proben dilatometriert, um diese Vermutung weiter zu bestätigen. Wie in Abb. ersichtlich ist, kann man keine besondere Ausdehnung in den Kurven bemerken. Vergleichsweise

wurde die Kurve der Gussproben mit der punktierten Linie gezeigt. Also ist die abnorme Ausdehnung beim Kokillguss nicht hervorgerufen durch den Abschreckeffekt.

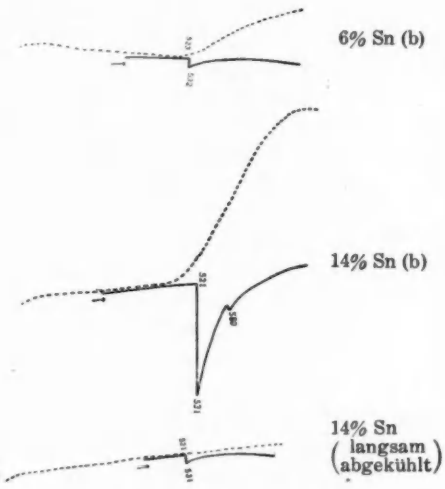


Abb. 6. Differentiale thermische Effekte der Bronzen.

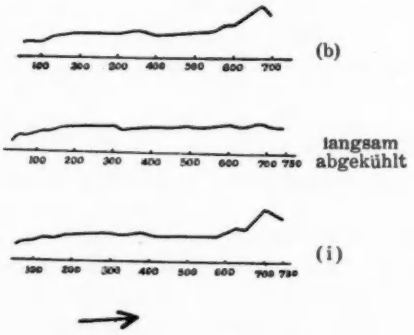


Abb. 7. Direkte Dilatationskurve der Bronzen (14% Sn).

Es wurden die thermischen Effekte während des Normalisierens des Gussgefüges auch untersucht. Abb. 6 zeigt die Wiedergabe der differentialthermischen Kurven, bei welchen reines Kupfer als Vergleichsprobe benutzt wurde; die punktierte Linie zeigt die Dilatationskurve.

Im Falle der Gussproben, welches 14% Zinn enthält, ist die spontane Wärmeabsorption bei etwa 520°C. aufgetreten; bei der ausgeglühten Probe ist sie aber sehr klein geworden. Es wurde deshalb sehr klar, dass die abnorme Ausdehnung der spontanen Wärmeänderung nicht unmittelbar zugrunde liegt.

Gemessen wurde auch die direkte Dilatationskurve bei 14% Zinn wie in Abb. 7; von 550°C. setzt die Ausdehnung bei gegossenen Proben plötzlich aus. Bei ausgeglühten Proben ist die Kurve ungefähr gleichlaufend mit der Temperaturachse.

Die elektrischen Widerstandsänderungen wurden bei den gegossenen sowie den normalisierten Proben auch untersucht. Wie in Abb. 8 ersichtlich ist, im Fall der Gussproben wird die Widerstandsteigerung allmählich schwächer bei etwa 490°C., und bei 520°C. dann bei etwa

650°C. fällt sie plötzlich ab. Bei normalisierter Proben tritt aber keine Änderung auf der kurve ein.

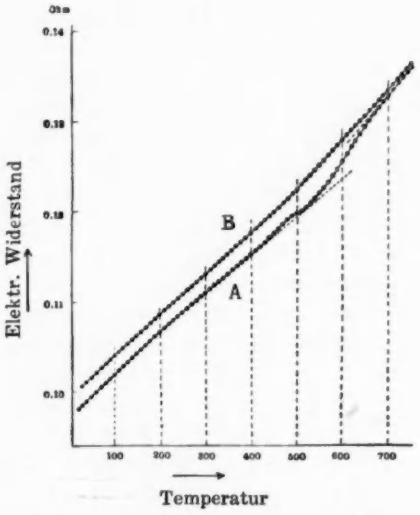


Abb. 8. Elektrischer Widerstand der gegossenen (A) und normalisierten (B) Bronzen (14% Sn).

Es wurden nun über die Beziehungen zwischen der spontanen Ausdehnung und der Diffusion der Gefügebestandteile weiter Versuche angestellt. Während der Dilatometrierung wurde die Gussprobe mit 10% Zinn im einzelnen für eine Stunde je bei 400°, 450° und 500°C. ausgeglüht. Unter Glühen bei 500°C. dehnt sich die Probe stark aus, wie in Abb. 9; bei 400°C. zieht sie sich vielmehr zusammen, aber bei 450°C. dehnt sie sich gleicherweise im Grad wie oben aus.

Man kann aus diesen Ergebnissen den Beginn der Ausdehnung bei etwa 425°C. bestimmen; beim Ausglühen bei 550°C. ist die Dilatationsänderung nach einer Stunde schon vollendet. Bei sandgegossenen ist aber 3 stundiges Ausglühen selbst bei 660°C. nötig, um die Ausdehnung vollenden zu lassen; bei 700°C. aber ist nur halbstündiges Ausglühen schon genug.

Abb. 10 zeigt die Wiedergabe der Dilatationskurve von 14%-zinnhaltiger Proben; bei 600°C. ist nach 2 Stunden die Ausdehnung fertig geworden, und bei 550°C. ist die Doppeldauer nötig. Bei Sandgussproben benötigt man 2½ Stunden selbst bei 700°C.

Abb. 11 zeigt das Mikrogefüge der in Gussform i gegossenen Proben mit 10% Zinn, welches durch die Ätzung in der alkoholischen Lösung von Ammoniumpersulfat hervorgerufen wurde; im Gefüge kann man die starke Seigerung deutlich erkennen. Ätzt man dieselbe Proben durch die Ferrichlorid-Lösung, erscheint die zweite Phase sehr klar wie in Abb. 12. Abb. 13. ist das Gefüge, welches bis 600°C. unter derselben Erhitzungsgeschwindigkeit geglüht wurde; die Seigerung ist etwas weniger geworden. Glüht man die Probe bis 750°C., verschwindet das Seigern beinahe (Abb. 14).

Die Mikrogefüge der Proben mit 14%igem Zinn wurden bei Abb. 15 bis 21 gezeigt; Abb. 15 ist das Gefüge der in Gussform i gegossenen

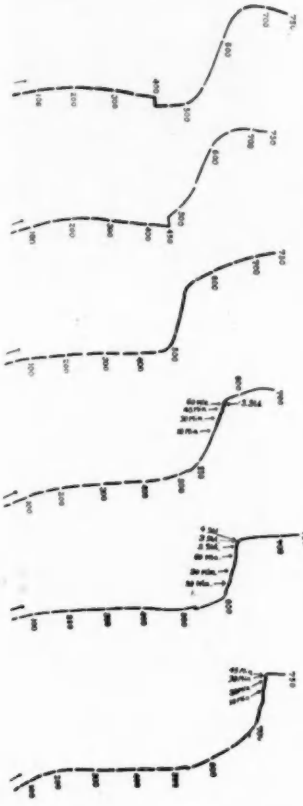


Abb. 9. Dilatationseffekte der 10% Sn bei konstanten Temperaturen.

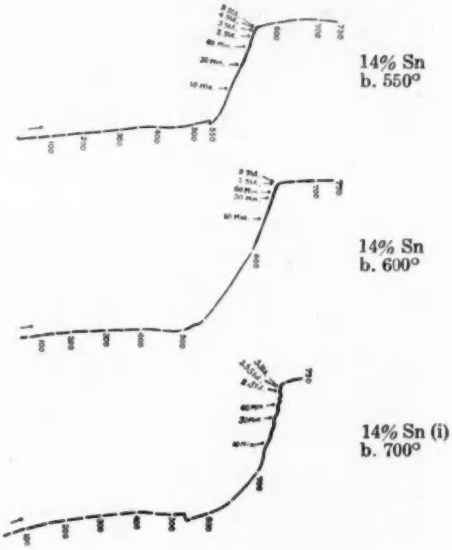


Abb. 10. Dilatationseffekte der 14% Sn bei konstanten Temperaturen.

Proben, und es wurde durch Ammoniumpersulfat-Lösung geätzt. Beim Ätzen der Ferrichlorid-Lösung wird die zweite Phase im Gefüge deutlich erkennbar wie Abb. 16. Bei der Erhitzung unterhalb 500°C. ist das Lösungsgehen von β-Phase schwer zu bemerken (Abb. 17). Erhitzt man auf ca. 700°C., löst sich derjenige beträchtlich im Grundphase auf (Abb. 18); selbst nach einstündigem Glühen, ist das Lösungsgehen noch immer nicht vollendet (Abb. 19). Abb. 20 zeigt das Gefüge der Proben, welches 3 Stunden bei derselben Temperatur geglüht wurde; es ist ganz homogen geworden.

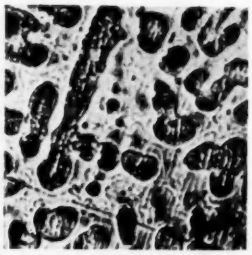


Abb. 11. 10% Sn

Abb. 12. 10% Sn

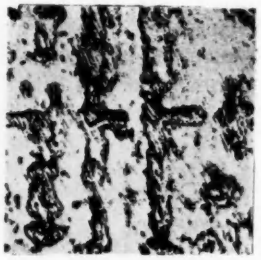


Abb. 13. 10% Sn (bei 600°)

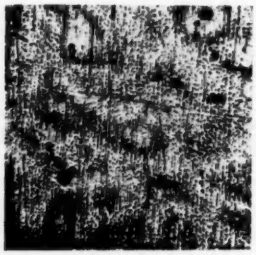


Abb. 14. 10% Sn (bei 750°)

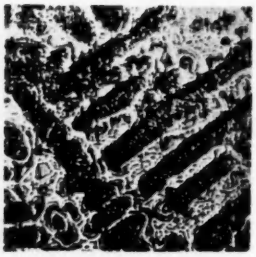


Abb. 15. 14% Sn

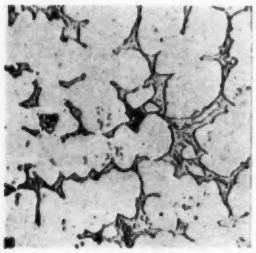


Abb. 16. 14% Sn

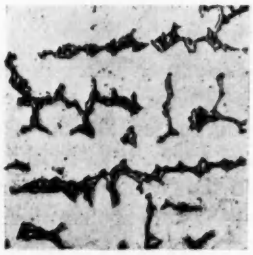


Abb. 17. 14% Sn (bei 500°)

Abb. 18. 14% Sn (bei 700°)

Abb. 19. 14% Sn (1 Std. bei 700°)

Abb. 20. 14% Sn
(3 Std. bei 700°)

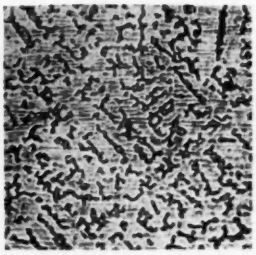


Abb. 21. 14% Sn

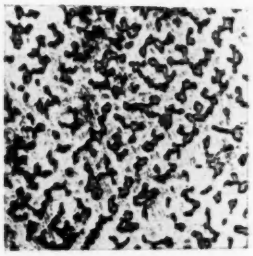


Abb. 22. 14% Sn
(bei 500°)

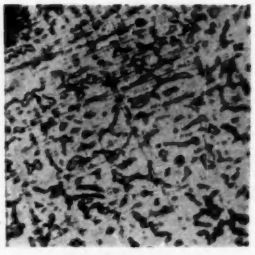


Abb. 23. 14% Sn
(bei 600°)

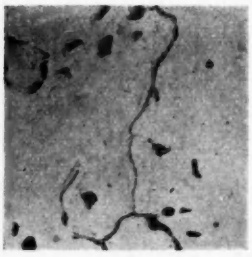


Abb. 24. 14% Sn
(1 Std. bei 600°)

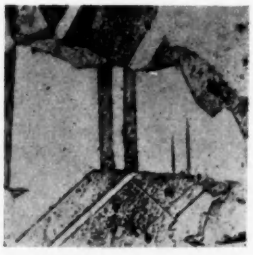


Abb. 25. 14% Sn
(2 Std. bei 600°)

Abb. 11–25. Vergrösserung: 200; Ätzmittel: Am. Persulfat oder Ferrichlorid.

Abb. 21 entspricht dem Gefüge der Proben, welche ins Gussform a gegossen wurde. Erhitzt man bis 500°C., werden die Körner von β-Phase ziemlich grösser (Abb. 22); beim Erhitzen bis 600°C. ist diese Phase durch Lösung beträchtlich weniger geworden (Abb. 23), und nach einstundigen Glühen ist das Gefüge fast homogen geworden (Abb. 24). Die weitere Erhitzung noch ein-stundenlang lässt das Gefüge vollkommen homogen werden (Abb. 25).

Man kann nun aus diesen Ergebnissen die engen Beziehungen zwischen der Dilatations- und der Gefügeänderung gut erkennen.

Man wird weiter hin den Diffusionsgrad der Gefügebestandteilen unmittelbare aus dem Ausdehnungsgrad vermuten können.